

**INVESTIGATION OF ATMOSPHERIC OZONE
IMPACTS OF SELECTED PESTICIDES**

**Research Proposal to the
California Air Resources Board**

by

University of California, Riverside
Center for Environmental Research and Technology
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ABSTRACT

The College of Engineering Center for Environmental Research and Technology (CE-CERT) proposes to carry out an experimental and computer-modeling study of the ground-level atmospheric ozone impact of at least four selected volatile pesticide compounds used in the State of California. The specific compounds to be studied will be determined in consultation with the ARB staff and appropriate advisory and stakeholder groups. For each compound studied environmental chamber experiments will be carried out to obtain data needed to develop and test chemical mechanisms that can be used in airshed models to estimate ozone impacts of the compounds in the atmosphere. The experiments will consist of “incremental reactivity” experiments to determine the effects of adding the compounds to various ambient surrogate organic - NO_x mixtures, using the approach we employed previously for developing and evaluating mechanisms for predicting ozone impacts of compounds. The chamber experiments will employ the state-of-the art facility developed under EPA funding for mechanism evaluation under controlled conditions that is being utilized in other studies for the CARB. The chemical mechanisms for the compounds will be developed to be consistent with the results of the experiments and other laboratory data, and will be incorporated either into the SAPRC-99 mechanism or the updated version being developed for the ARB. These mechanisms will then utilized to calculate the estimated ozone impacts of the compounds in the MIR and other appropriate ozone reactivity scales. Effects of mechanism uncertainties in the ozone impacts will be assessed, and uncertainty ranges for MIR and other reactivity estimates will be assessed for all the compounds studied. Mechanisms and reactivities for other volatile pesticide VOCs used in California will be estimated where feasible. The amount requested is \$99,850, and the period of performance is March 1, 2005 through February 28, 2006.

CONTENTS

BACKGROUND AND PROBLEM STATEMENT	4
Quantification of Ozone Impacts.....	4
Current Mechanisms for Ozone Impact Assessment of Individual VOCs.....	5
Ozone Impact Research Needs for Pesticide VOCs.....	9
OBJECTIVES AND OVERALL APPROACH	15
APPROACH	16
Selection of Compounds	16
Environmental Chamber Studies.....	17
Facility Description	17
Experiments to be Carried Out	18
Mechanism Development and Evaluation.....	23
Ozone Impact Assessments	24
REPORTING AND DELIVERABLES.....	25
SCHEDULE.....	25
BUDGET	26
RELATED PROGRAMS	28
Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions	28
Environmental Chamber Studies of VOC species in Architectural Coatings and Mobil Source Emissions	28
Updated Chemical Mechanisms for Airshed Model Applications.....	29
Utilization of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Evaluation.....	30
REFERENCES	32
BIOGRAPHICAL SKETCH	36

BACKGROUND AND PROBLEM STATEMENT

Pesticides are widely used in agricultural operations in California and in addition to their other environmental impacts they may also be emitted into the atmosphere and contribute to the formation of ground-level ozone. Because ground-level ozone continues to be a problem in many areas of California, the California Air Resources Board (ARB) and the California Department of Pesticide Regulation need a means to quantify the ozone impacts of pesticide compounds that are used in the state. As discussed below, progress has been made in developing methods to estimate and quantify relative ozone impacts of the major classes of VOCs present in vehicle emissions and solvents, but the ozone impacts of most of the compounds used in pesticides are unknown. A research program designed to address this is discussed in this proposal. Before describing the specifics of this proposed program, it is useful to describe the methods currently used to quantify ground-level ozone impacts of VOCs, and the types of information that is needed to apply these methods to pesticide compounds. This is discussed in the sections below.

Quantification of Ozone Impacts

Many different types of volatile organic compounds (VOCs) are emitted into the atmosphere, where they can affect photochemical ozone formation and other measures of air quality. Because VOCs can react in the atmospheres at different rates and with different mechanisms, the different types of VOCs can vary significantly in their effects on air quality. An ability to quantify the effects of emissions of different types of VOCs on ozone formation is useful for assessing relative ozone impacts of various emissions sources such as pesticide use, and for developing cost-effective ozone control strategies. The effect of a VOC on ozone formation in a particular environment can be measured by its “incremental reactivity”, which is defined as the amount of additional ozone formed when a small amount of the VOC is added to the environment, divided by the amount added. Although this can be measured in environmental chamber experiments, incremental reactivities in such experiment cannot be assumed to be the same as incremental reactivities in the atmosphere (Carter and Atkinson, 1989; Carter et al., 1995a). This is because it is not currently practical to duplicate in an experiment all the environmental factors that affect relative reactivities; and, even if it were, the results would only be applicable to a single type of environment. The only practical means to assess atmospheric reactivity, and how it varies among different environments, is to estimate its atmospheric ozone impacts using airshed models.

However, airshed model calculations are no more reliable than the chemical mechanisms upon which they are based. While the initial atmospheric reaction rates for most VOCs are reasonably well known or at least can be estimated, for most VOCs the subsequent reactions of the radicals formed are complex and have uncertainties that can significantly affect predictions of atmospheric impacts. Laboratory studies can reduce these uncertainties, but for most VOCs they will not provide the needed information in the time frame required for current regulatory applications. For this reason, environmental chamber experiments and other experimental measurements of reactivity are necessary to test and verify the predictive capabilities of the chemical mechanisms used to calculate atmospheric reactivities.

Therefore, experimental measurements of reactivity play an essential role in ozone impact quantification. They provide the only means to assess as a whole all the many mechanistic factors that might affect reactivity, including the role of products or processes that cannot be studied directly using currently available techniques. Because of this, the ARB and others have funded programs of environmental chamber studies to provide data needed to reduce uncertainties in ozone impact assessments of the major classes of VOCs present in emissions, and the data obtained were used in the development of the most recent mechanism for deriving ozone reactivity scales (see Carter, 2000 and references therein). Although there has been significant progress, the number of compounds that were

adequately studied do not represent all of those presently in the emissions inventories, and in particular do not represent many classes of compounds used for pesticides, as is discussed in more detail below.

Current Mechanisms for Ozone Impact Assessment of Individual VOCs

Although several chemical mechanisms are used in airshed modeling applications in the United States (Gery et al, 1988, 1989; Stockwell et al, 1990, 1997; Carter, 2000a,b), the SAPRC-99 mechanism (Carter, 2000) is considered to represent the current state of the art for model simulations of ozone impacts of individual VOCs. This is because it is the only one of these mechanisms that is designed to separately represent the reactions of several hundreds of different types of VOCs, while most other mechanisms use a limited number of “lumped species” to represent a broad classes of compounds assumed to have similar reactivity. It is also the most comprehensively evaluated against available chamber data for the representative compounds for which such data are available. The only other currently available state of the art mechanism that can be used to assess impacts of multiple VOCs is the European “Master Chemical Mechanism” (MCM) (Jenkin et al, 1997, 2003; Saunders et al, 2003, MCM, 2004), which explicitly represents the tropospheric degradations of over 130 volatile organic compounds. However, the current version of the MCM does not represent as many different VOCs as SAPRC99 and has not been as comprehensively evaluated against available chamber data. In addition, the highly explicit form of the mechanism is not compatible with airshed modeling software used in California. Therefore, in this discussion we will focus on the current version of the SAPRC mechanism. However, much of what is stated below will be applicable at least to some extent to the MCM.

The types of VOCs that are currently represented in the SAPRC-99 mechanism are listed on Table 1. The table also includes the number of compounds of each type that are separately represented in the mechanism (excluding those represented by other compounds or generic species using the “lumped molecule approach”), and the number of compounds for which environmental chamber data are available and have been used for mechanism development or evaluation. The table also gives the range of SAPRC-99 uncertainty codes assigned for the compounds. These uncertainty codes, which are shown on Table 2, represent subjective estimates of the mechanism developer of the approximate range of uncertainty in the mechanism and the corresponding ozone impact estimates, and the likelihood that the ozone impact estimate may change significantly if new data become available concerning the compound’s mechanism. Note that uncertainty codes of 4 or greater indicate sufficient uncertainty that upper limit reactivity estimates (Carter, 2000, Appendix D) may be appropriate for some regulatory applications.

The best studied compounds are the alkanes, alkenes, aromatics and simple alcohols that are important in vehicle exhausts and the oxygenated compounds such as alcohols glycols, glycol ethers, etc, that are used in solvents. There are also data and mechanisms for the major biogenic compounds isoprene and selected terpenes. For most non-aromatic hydrocarbons and oxygenated compounds the SAPRC-99 mechanism generation and estimation system has been found to perform reasonably well in generating mechanisms that give fair fits to chamber data in most cases without significant adjustment (Carter, 2000, Carter et al, 2000a). The mechanism generation system cannot be used for terpenes and aromatics but parameterized mechanisms give fair fits to the available data. The mechanisms for aromatics are highly uncertain, but sufficient chamber data exists for various types of aromatic hydrocarbons (up to C₉) to derive parameterized mechanisms that fit results of reactivity experiments. Although recent data indicate that there are compensating errors in the aromatics mechanisms (Carter, 2004a), available data suggest that it is more likely that this is more likely to have effects on predictions of the base mechanism than predictions of relative reactivities of these compounds.

The available data and mechanisms become much more limited for compounds other than the hydrocarbons and oxygenates discussed above. The only chlorine-containing compound for which chamber data are available and a mechanism has been developed is chloropicrin (Carter et al, 1997a), and

Table 1. Summary of types of VOCs represented in the current SAPRC-99 mechanisms and associated types of mechanisms and uncertainties.

Type	Cmpds [a] Total Cham.		Derivation of Mechanism [b]	Comments	Unc'y Codes [c]
Alkanes	125	17	Generated	Mechanisms most uncertain for highly branched high molecular weight compounds	1 - 3
Monoalkenes	65	6	Generated	No data to test mechanism for compounds >C ₆ .	1 - 4
Dialkenes	2	1	Assigned and Generated	Data available only for isoprene. 1,3-Butadiene mechanism estimated by analogy	1 - 3
Terpenes	5	5	Parameterized	Mechanisms derived only for individual terpenes where chamber data available. Reactivity estimates for other compounds much more uncertain.	2 - 3
Styrenes	1	1	Parameterized	Only styrene itself is represented	2
Aromatic hydrocarbons	16	12	Parameterized	Data are available for benzene, the C ₇ -C ₉ methylbenzene isomers, ethylbenzene, naphthalene, and 2,3-dimethylnaphthalene. Extrapolation of parameters adjusted to fit data for one compound to estimate a mechanism for another is highly uncertain.	2 - 3
Acetylenes	4	1	Assigned	Explicit acetylene mechanisms derived and adjusted to fit chamber data. Other acetylene mechanisms derived by analogy, and are more uncertain.	2 - 4
Alcohols, ethers, glycols, esters, alcohol ethers, etc.	216	25	Generated	The mechanism generation system appears to perform reasonably well in deriving mechanisms that give reasonable fits to the data for these types of compounds with little or no adjustment.	1 - 3
Carboxylic Acids	11	0	Generated	The performance of the mechanism generation system in deriving mechanisms for this class of compounds is not adequately evaluated. Greatest uncertainty is for unsaturated acids.	3 - 5
Unsaturated oxygenates	18	3	Generated	Data available only for acrolein, methacrolein and methyl vinyl ketone. Estimated mechanisms are considered uncertain.	1 - 5
Simple aldehydes and ketones	41	8	Generated	Highest uncertainties assigned to cyclobutanone and cyclopentanone. Others with no data assigned uncertainty code of 3.	1 - 4
Aromatic photooxidation products	6	2	Parameterized or Assigned	Limited data available only for benzaldehyde and cresols. Other compounds are the α -dicarbonyls.	2 - 4

Table 1 (continued)

Type	Cmpds [a] Total	Cham.	Derivation of Mechanism [b]	Comments	Unc'y Codes [c]
Other aromatic oxygenates	1	0	Parameterized	Phenoxyethanol only such compound currently represented. Mechanism estimated by analogy with aromatic hydrocarbons	4
Nitro aromatics	1	0	Parameterized	Nitrobenzene only such compound currently represented. Mechanism estimated by analogy with aromatic hydrocarbons	6
Amines and alcohol amines	7	0	Placeholder	"Placeholder" mechanism not suitable for reactivity estimates of individual compounds	6
Aromatic isocyanates	3	2	Parameterized	Data for TDI and a model compound used to represent MDI indicate that these compounds are inhibitors.	2 - 3
Miscellaneous N-Containing	1	1	Assigned	Data and mechanism for N-methyl-2-pyrrolidone only.	2
Halogenated hydrocarbons	22		Placeholder	"Placeholder" mechanism not suitable for reactivity estimates of individual compounds	6
Chloropicrin	1	1	Assigned	Not represented in standard mechanism because it requires chlorine chemistry.	
Volatile methyl siloxanes	3	3	Parameterized	Not represented in standard mechanism because it requires nonstandard product species.	
S-containing compounds	2	1	Assigned	DMSO only such compound currently represented.	2

[a] Number of compounds represented in the mechanism ("Total") and for which environmental chamber data are available for mechanism evaluation ("Cham").

[b] Derivation of mechanism. Codes used are as follows:

Generated..... Mechanism derived using the SAPRC-99 mechanism generation system as described by Carter (2000a). A computer program generates a fully explicit mechanisms using measured (where available) or estimated rate constants and branching ratios, and these are used to derive mechanisms in terms of SAPRC-99 model species. Some uncertain branching ratios are adjusted to fit chamber data for certain compounds.

Assigned..... Reactions are assigned based on available mechanistic information. Uncertain portions adjusted to fit chamber data if needed.

Parameterized.. A simplified or parameterized mechanism is used to represent the overall effects of portions of the mechanism that are unknown or too complex to derive explicitly. Parameters are adjusted to fit chamber data where appropriate.

Placeholder..... a highly simplified "placeholder" mechanism used to permit representation in emissions. The measured OH rate constant is used where available, but the calculated mechanistic reactivities are uncertain and probably not correct

[c] Uncertainty codes assigned to mechanism in the MIR tables of Carter (2000a). Uncertainty codes are given in Table 2.

Table 2. Uncertainty codes used with SAPRC-99 mechanism and reactivity assignments.

Code	Description
1	Considered to be relatively uncertain, or some uncertainties but reactivity is not expected to change significantly.
2	Uncertain mechanism may change somewhat if refined, but change is expected to be less than a factor of two. If the compound is predicted to inhibit O ₃ , changes are not expected to affect predicted inhibition, but may affect magnitude of inhibition. This code is also used for compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
3	Uncertain and may change if compound is studied (or studied further) or estimation methods are updated. Change in MIR could be as much as a factor of two. This code is also used for (1) compounds whose reactivities are expected to be sensitive to the representation of the reactive products, whose accuracy is difficult to test experimentally and (2) compounds whose reactivities are expected to be highly sensitive to ambient conditions or to changes in the base mechanism.
4	Uncertain and is expected to change if compound is studied or estimation methods are updated. It is recommended that uncertainty adjustments be employed in regulatory applications.
5	Non-negligible chance of the estimate being incorrect in significant respects. It is recommended that uncertainty adjustments be employed in regulatory applications.
6	Current mechanism is probably incorrect, but biases in atmospheric reactivity predictions are uncertain. It is recommended that uncertainty adjustments be employed in regulatory applications.

appropriately representing its impact requires including chlorine chemistry in the mechanism, which is not currently part of the base mechanism used to calculate MIR and other reactivity scales (Carter, 2000a). This is not representative of the halogenated alkanes, alkanes, and aromatics, which are either not represented in the current mechanism or are represented by “placeholder” mechanisms whose appropriateness for reactivity assessment is highly uncertain. Some chamber and laboratory data have been obtained for propyl bromine other bromine species (Carter et al, 1997b, Carter and Tuazon, 2000), but no mechanism was developed that was consistent with the data, so no bromine-containing compounds are currently represented. The only nitrogen-containing compound represented in the current mechanism (other than organic nitrates or nitroaromatic photooxidation products that are represented by lumped model species) is N-methyl-2-pyrrolidone (Carter et al, 1996), and a few aromatic isocyanates (Carter et al, 1997c, 1999), and the only sulphur-containing compound currently represented is DMSO (Carter et al, 2000b). The data and mechanisms for these compounds are not sufficient to serve as a basis for estimating mechanism for other nitrogen or sulfur-containing VOCs.

Therefore, if relative ozone reactivity assessments are needed for halogenated, nitrogen- or sulfur-containing VOCs other than the few that have been studied already then mechanisms need to be developed for those compounds, and new environmental chamber data are needed to develop and evaluate those mechanisms. Ideally these mechanisms should be based on laboratory studies of the kinetics and mechanisms of the major reactions involved (and those of the major reactive photooxidation products, where applicable. However, chamber data could serve as a basis for deriving parameterized mechanism that could estimate ranges of likely impacts of the compounds even if other mechanistic information is not available. At a minimum, chamber data could be used to determine if the compounds are radical inhibitors or initiators.

Ozone Impact Research Needs for Pesticide VOCs

Table 3 shows the VOC speciation profile that is used to represent pesticide emissions in the 2000 California VOC emissions inventory. The approximate mass fractions, which represent the relative amounts of each compound that are estimated to be emitted, are also shown, with the compounds listed in order of decreasing amounts emitted. The chemical structure, volatility, and the representation of the compounds in the current SAPRC-99 mechanism, and the SAPRC-99 uncertainty classification, if applicable, are also shown. The list includes several complex hydrocarbon mixtures such as “aromatic 200 solvent” and “kerosene”. These are not discussed further here except to note that the ozone impacts of representative petroleum distillates are currently being studied as part of our ongoing study of the ozone impacts of architectural coatings VOCs (see Related Programs, below, and Carter, 2004c), and methods to estimate their ozone impacts already exist (Kwok et al, 2000). For this proposal we will focus on the individual compounds on the list for which reactivity data and estimates are most needed.

It is immediately apparent that most of the pesticide VOCs listed on Table 3 are either not represented in the current mechanism or are represented in a highly approximate and uncertain manner. The compounds that have been studied, in order of mass fraction, are chloropicrin (Carter et al, 1997a), methyl isobutyl ketone (Carter et al, 2000a), acrolein (Carter, 2000a), propylene glycol (Carter et al, 1997d), and NMP (Carter et al, 1996). Additional experiments with propylene glycol are also being carried out as part of our ongoing coatings reactivity project (Carter, 2004c). An estimated mechanism for glycerol was derived using the mechanism generation system (Carter, 2000a), and although no experimental data exist to support this mechanism its uncertainty is not considered to be on the same order as those for the other compounds discussed below.

Given below is a brief discussion of the compounds listed on Table 3 for which reactivity data may be needed. Note that although we believe that there are no available environmental chamber experiments for these compounds suitable for evaluating mechanisms for ozone formations, we have not yet carried out a comprehensive literature search for other relevant kinetic and mechanistic information for these compounds. Therefore the discussion of available information may be incomplete. Obviously such information would need to be incorporated in any mechanism developed for these compounds.

The first compound on the list is methyl bromide, which is currently represented using a “placeholder” mechanism that probably does not correctly represent its mechanistic reactivity. However, the rate constant for its reaction with OH radicals, which is expected to be its major atmospheric fate, has been measured to be only $4 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$, indicating that regardless of its mechanism it may have only a relatively low impact on O₃. Representing it in the current mechanism may be a problem because it is expected to release Br atoms when it reacts, and our previous experience with attempting to develop mechanisms for bromine species was not successful (Carter et al, 1997b, Carter and Tuazon, 2000). However, it may be appropriate to do an upper limit reactivity estimate for this compound to determine whether developing an improved mechanism for this compound should be a priority.

After methyl bromide the most important compound according to Table 3 is methyl isothiocyanate (MITC). Although no environmental chamber data are available for this compound, there have been studies of its environmental fate (Wales, 2002, and references therein). Geddes et al (1995) determined that MITC undergoes photodecomposition in simulated sunlight with a half life of about one day, suggesting that its atmospheric reactivity is probably non-negligible. However, the impacts of the subsequent reactions on O₃ formation has not been determined, though a literature search may reveal relevant information concerning its subsequent reactions and the reactions of its major products. It may be possible to derive a mechanism for this compound based on available data and estimates, but environmental chamber data would still be needed to evaluate it. The compound is sufficiently volatile

Table 3. Pesticide speciation profile from the 2000 California VOC emissions inventory.


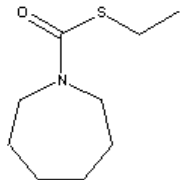
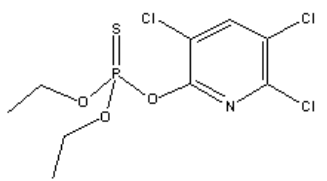
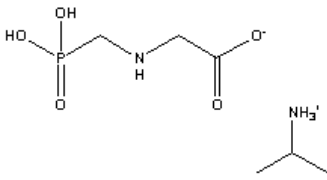
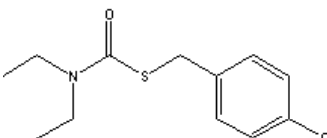
Compound or Mixture [a]	CAS #	Mass fract. [a]	Vapor Pressure (ppm) [b]	SAPRC-99 [c]		Structure [d]
				Model Species	Unc. Code	
methyl bromide	74-83-9	25.3%	high	ME-BR	6	CH ₃ Br
MITC (methyl isothiocyanate)	556-61-6	17.8%	high			CH ₃ NCS
1,3-dichloropropene	542-75-6	11.3%	high			
chloropicrin	76-06-2	8.6%	high	CCL3NO2	[e]	CCl ₃ NO ₂
aromatic 200 solvent		4.8%				Hydrocarbon mixture
xylene range solvent		4.6%				Hydrocarbon mixture
molinate	2212-67-1	3.3% [f]	7.4			
kerosene		1.7%				Hydrocarbon mixture
chlorpyrifos	2921-88-2	1.7%	0.03			
methylisobutyl ketone	108-10-1	0.8%	high	MIBK	2	CH ₃ C(O)CH ₂ CH(CH ₃)CH ₃
glyphosate, isopropylamine salt	38641-94-0	0.7%	[g]	NONVOL	[h]	
acrolein	107-02-8	0.7%	high	ACROLEIN	3	CH ₂ =CHCHO
glycerine	56-81-5	0.5%	0.22	GLYCERL	2	HOCH ₂ CH(OH)CH ₂ OH
propylene glycol	57-55-6	0.5%	170	PR-GLYCL	1	CH ₃ CH(OH)CH ₂ OH
thiobencarb	28249-77-6	0.5%	0.03			

Table 3 (continued)

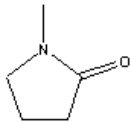
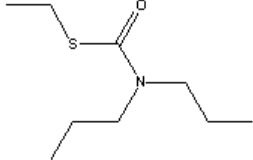
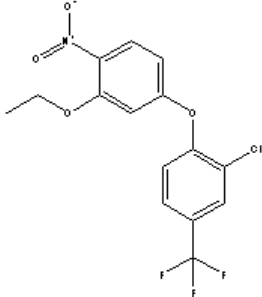
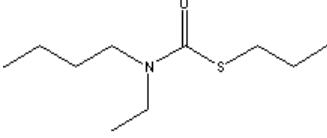
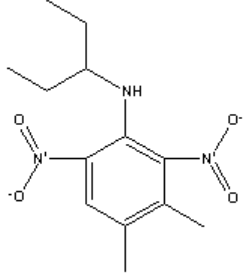
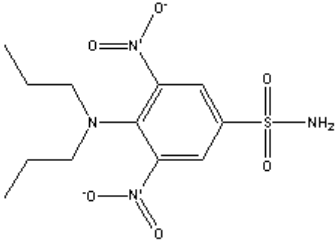
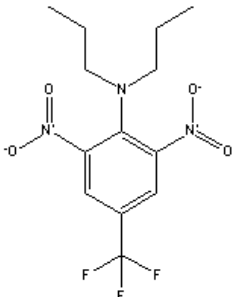
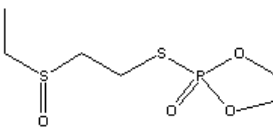
Compound or Mixture [a]	CAS #	Mass fract. [a]	Vapor Pressure (ppm) [b]	SAPRC-99 [c]		Structure [d]
				Model Species	Unc. Code	
N-methyl pyrrolidinone	872-50-4	0.5%	454	NMP	2	
EPTC	759-94-4	0.5%	32			
oxyfluorfen	42874-03-3	0.5%	0.0003	NONVOL	[h]	
pebulate	1114-71-2	0.4%	116			
pendimethalin	40487-42-1	0.4%	0.04			
oryzalin	19044-88-3	0.3%	0.00001	NONVOL	[h]	

Table 3 (continued)

Compound or Mixture [a]	CAS #	Mass fract. [a]	Vapor Pressure (ppm) [b]	SAPRC-99 [c]		Structure [d]
				Model Species	Unc. Code	
trifluralin	1582-09-8	0.2%	0.06			
aliphatic solvent		0.2%				Hydrocarbon mixture
oxydemeton-methyl	301-12-2	0.2%	0.04			

[a] Mass Fraction of compound in total pesticide VOC profile. Data provided by Frank Spurlock of the California Department of Pesticide Regulation on October 18 to the staff of the California Air Resources Board and provided to us by Dongmin Luo of the CARB. The unidentified fraction, which consists of 13.9% of the mass of the profile, is not shown.

[b] Vapor pressure in mm HG at 25°C obtained from the Syracuse Research Corporation (SRC) online physical properties database. Available at <http://www.syrres.com/esc/physdemo.htm>, accessed October, 2004. Converted to ppm using 1315 ppm per torr. "High" means that the vapor pressure is greater than 1000 ppm.

[c] Model species used to represent compound in the current SAPRC-99 mechanism and assigned uncertainty code. (See Table 2 for the meanings of the uncertainty codes.) If these compounds are blank then the compound is not currently represented in the mechanism.

[d] Structure graphics obtained from the ChemFinder online database (<http://chemfinder.cambridgesoft.com>)

[e] This compound is not part of the standard SAPRC-99 mechanism because it requires chlorine chemistry to be represented. No uncertainty code assigned, but it is probably equivalent to 2 or 3 when chlorine chemistry is implemented.

[f] Use of this compound is being phased out.

[g] Vapor pressure data not available from the SRC online database.

[h] This compound is represented as non-volatile in the current emissions speciation database (Carter, 2004b).

that it should not be difficult to study in environmental chamber experiments. Therefore, this is clearly a good candidate for mechanism development and environmental chamber studies.

The next compound after MITC on Table 3 is 1,3-dichloropropene, which is also sufficiently volatile to be relatively straightforward to study in environmental chamber experiments. Although a gas-phase mechanism for ozone reactivity assessment has not been developed for this compound, as discussed by Finlayson-Pitts and Pitts (1997) there are kinetic and product data available for the atmospheric reactions of this compound. Information and estimates may be available to derive a mechanism for evaluation, though we suspect that available information is incomplete and available estimates may be necessary. In any case, such a mechanism will have uncertainties and will need to be evaluated with well-characterized environmental chamber experiments. It may be necessary to include chlorine chemistry in the base mechanism for this compound; this will depend on the extent to which chlorine atoms are released when the compound reacts.

The other previously unstudied compounds listed on Table 3 consist of various sulphur-, nitrogen- and in some cases chlorine and phosphorous-containing compounds with varying degrees of volatility. Atkinson (personal communication) is studying the atmospheric reactions of some phosphorous-containing model compounds that may be relevant to estimating mechanisms for some of these pesticides, and data for selected thiocarbamates are available as discussed below, but we suspect that other relevant gas-phase mechanistic information is extremely limited. It is probable that in many cases it may be necessary to develop parameterized mechanisms and adjust the uncertain parameters to fit environmental chamber data relevant to atmospheric conditions. In any case, we do not believe that chamber data are available for deriving or evaluating mechanisms of any type.

The issue of volatility needs to be taken into account in considering (a) whether it is feasible to carry out environmental chamber experiments suitable for mechanism evaluation and (b) whether the compound actually exists in sufficient concentration in the atmosphere to participate in ozone formation. Although an assessment of availability issues is beyond the scope of this proposal, we suspect that if a compound is sufficiently volatile that it is feasible to carry out gas-phase environmental chamber experiments suitable for evaluation of ozone formation mechanisms, it is likely to undergo such gas-phase reactions in the environment. Note that the inverse is not necessarily true. The surface/volume ratio in even the largest chambers is much greater than in the atmosphere, and semi-volatile or “sticky” compounds that go to the walls in chamber experiments may still react in the gas phase in the environment.

Although we have not investigated the limit of low vapor pressure for compounds for chamber studies, from a thermodynamic standpoint we would place the absolute lower limit at about 0.1 ppm at ambient temperatures (25°C). Concentration in this range are usually necessary to see a measurable effect on environmental chamber experiments. This rules out chamber studies of chlorpyrifos, glyphosate isopropylamine salt, thiobencarb, oxyfluorfen, pendimethalin, oryzalin, trifluralin, and oxydemeton-methyl, and suggests that experiments with glycerine (which is expected to be very “sticky” in addition to having borderline volatility) are unlikely to be successful.

This leaves, in order of importance on Table 3, molinate, EPTC and pebulate, whose structures are shown below. All three of these compounds are thiocarbamates, i.e., have structures of the general type $R_2N-CO-S-R$, where “R” is an alkyl group (see Figure 1). Kwok et al (1992) obtained reasonably comprehensive kinetic and some mechanistic information on EPTC and also dimethylthiocarbamate and cycloate, whose structures are also shown on Figure 1. Although molinate and pebulate were not studied, the data for the other compounds can provide a basis for estimating rate constants and mechanism for thiocarbamates in general. The rate constants they obtained indicate that these compounds should have non-negligible atmospheric reactivity. However, environmental chamber experiments would be needed to

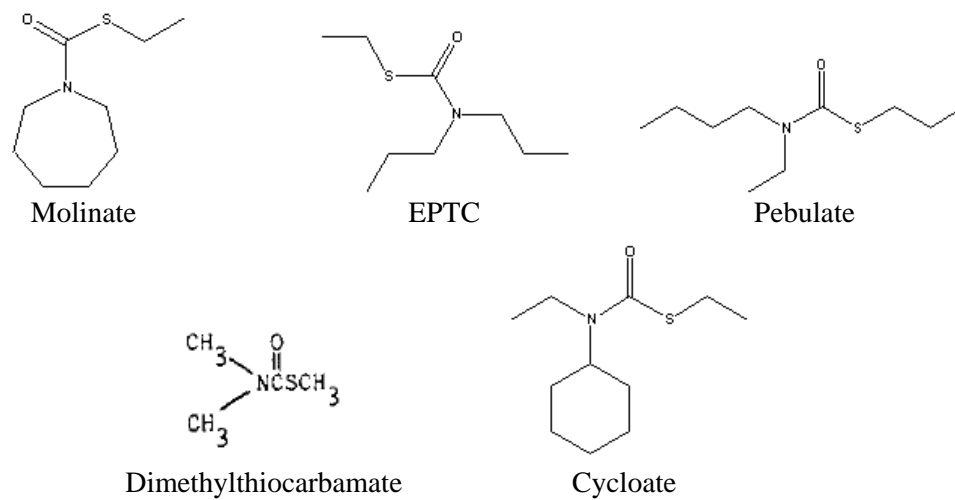


Figure 1. Structures of the thiocarbamate pesticides and of the model compounds studied by Kwok et al (1992)

evaluate the predictive capability of the mechanism, particularly with regard to the contribution of any reactive products to the overall reactivity.

OBJECTIVES AND OVERALL APPROACH

The objective of this project is to develop methods for estimating and quantifying ozone impacts for selected pesticide compounds for which such estimates are not currently available. At least four compounds will be selected for study after consultation with the California ARB and Department of Pesticide Regulation staff and appropriate stakeholder groups, but based on the discussion above and preliminary feedback from CARB staff it is expected that they would include MITC, 1,3-dichloropropene, and EPTC. The specific objectives will be as follows:

- Conduct environmental chamber experiments whose data can be used to test model predictions of the effects of the selected compound on O₃ formation, radical levels, and other measures of reactivity in a range of simulated atmospheric conditions. Simpler, more volatile model compounds may be studied if it is found not to be feasible to study a specific compound of interest.
- Develop atmospheric chemical mechanisms for the compounds that can be used to predict their atmospheric ozone impacts and are consistent with available kinetic and mechanistic data and that can predict the results of the environmental chamber experiments.
- Estimate mechanism for other pesticide compounds that have not been studied but are chemically similar to those that will be or have been studied or for which sufficient relevant data may be available in the literature. Develop estimated mechanisms for other volatile pesticide compounds that can be used to estimate approximate ozone impacts.
- Incorporate the mechanisms developed for this project into the latest version of the detailed SAPRC mechanism (SAPRC-99 or an updated version being developed for ARB project 03-318) and calculate the ozone impacts in the MIR and other appropriate reactivity scales. The chlorine chemistry module being developed for that project will be utilized when necessary. Evaluate the effects of the uncertainties in these mechanisms on ozone reactivity quantifications.
- Make recommendations on how the reactions of pesticide compounds of interest should be represented in airshed models and on additional laboratory or chamber studies needed to reduce uncertainties in ozone impacts of pesticide emissions.

The approach will be similar to that we have successfully employed in previous studies for compounds in mobile source and solvent emissions, for which ozone reactivity estimates are already available. The compounds studied will be added to the list of compounds in the MIR tables used in California and elsewhere, along with their associated uncertainty classifications.

APPROACH

Selection of Compounds

Based on considerations discussed above, we are proposing to conduct environmental chamber experiments and develop mechanisms for MITC, 1,3-dichloropropene, EPTC, and additional compounds if time and resources permit. Although molinate may also be appropriate for study, our current feedback is that it is being phased out and therefore it is probably of lower priority. However, this list is not finalized and we will meet with California ARB and Department of Pesticide Regulation staff and appropriate stakeholder groups to review this list and receive recommendations for modifications if appropriate. The format and timing of the meetings will be determined by the CARB staff, but it is expected that the initial meeting will be held in the Spring of 2005, around the beginning of the period of performance for this project. We will communicate to the staff and stakeholders the experimental and mechanistic issues involved, and the types of compounds most likely to yield useful data, while they will communicate to us their priorities from a regulatory and industry standpoint. The budget for this project includes two trips to Sacramento to meet with the staff and stakeholders, at least one of which is expected to concern the selection of compounds to be studied.

Note that because of handling of analytical problems caused by low volatility, “stickiness” it may be determined that it is not experimentally feasible to conduct useable environmental chamber experiments for all the compounds given priority for study. Experimental difficulties are not expected to be the case for MITC and 1,3-dichloropropene but may possibly be the case for molinate and almost certainly will be a problem for the compounds with 25°C vapor pressures of less than 0.1 ppm. If improved reactivity estimates for such compounds are determined to be a sufficient priority, we may conduct experiments with higher vapor pressure model compounds with similar structural groups to test mechanisms for reactions of the general type of compound. This will be determined only after discussion with the staff and stakeholder groups as discussed above.

Some of the low volatility pesticide compounds may be chemically converted to more volatile compounds in the soil or water, and these transformation compounds may then be emitted into the atmosphere. An assessment of this aspect of pesticide chemistry is beyond the scope of this project. However, if the CARB staff and stakeholder groups believe that such transformations are likely in the case of a pesticide of interest, it may be appropriate to study the atmospheric chemistry of the transformation compound. This will be determined after discussion with the CARB staff and stakeholder groups, and we expect their recommendations will reflect input from appropriate experts in chemistry of the compounds in the soil or water environment where they are applied.

The CARB staff and stakeholder groups may also conclude that studies of solvents such as Aromatics 200, kerosene, or xylene solvent should be a priority for this project. Note that we can study or make ozone impact estimates of these solvents only if the CARB staff or a CARB-approved stakeholder or industry group provides us with the chemical compositions of these solvents with sufficient detail for representation in the mechanism¹, and can provide us with representative analyzed samples for study. We will make recommendations as to whether the available information and mechanistic uncertainty is such that experimental studies of these solvents are appropriate for this project, and include studies of such solvents in this project if appropriate.

¹ For alkane constituents, carbon number and type (normal, branched, or cyclic) information is generally sufficient, though more detail may be required for “Isopar” type solvents (Carter et al, 2000c). Compositions in terms of individual compounds are generally desirable for aromatic constituents.

Environmental Chamber Studies

The types of environmental chamber experiments useful for mechanism evaluation have been discussed previously (e.g., see Carter et al, 1996, 1997a, 2000a,b, Carter, 2000a) and are being utilized in our current study of ozone reactivity of architectural coatings VOCs (see Related Programs, below). For most compounds the most useful data is obtained using “incremental reactivity” experiments, where the effects of adding the test compound to “base case” reactive organic gas (ROG) surrogate - NO_x mixtures is determined. The base case mixture is derived to be a simplified representation of the compounds present in ambient pollution episodes in which ozone formation occurs, and provides a chemical environment representative of that where the compounds will react and affect ozone formation. Experiments using at least two different reactive organic gas (ROG) /NO_x ratios will be carried out for each compound to test mechanisms under different chemical conditions. Other experiments may be conducted as appropriate that it is determined that they may be useful for testing or deriving specific aspects of the mechanism for individual compounds. The chamber and instrumentation to be employed, and the specific experiments to be carried out, are discussed further below.

Facility Description

The environmental chamber experiments will be carried out using the new UCR EPA chamber, which is described in more detail elsewhere (Carter, 2002, 2004a,d). This chamber was constructed under EPA funding to address the needs for an improved environmental chamber database for mechanism evaluation (Carter, 1999, see also Related Programs, below). The objectives, design, construction, and initial evaluation of this chamber facility are described in more detail elsewhere (Carter et al, 1999, Carter, 2002a, 2004a,d). This chamber was successfully utilized in our recently-completed “low NO_x” mechanism evaluation study for the CARB (ARB contract number 01-305; Carter, 2004a) and is currently being used for soon-to-be-completed study of ozone impacts of selected coating VOCs (ARB contract no. 00-333; Carter, 2004c), and the report or web site for these projects can be consulted for more details. A brief description of the chamber and the procedures we expect to employ is given below.

The UCR EPA chamber consists of two ~85,000-liter Teflon® reactors located inside a 16,000 cubic ft temperature-controlled “clean room” that is continuously flushed with purified air. The clean room design is employed in order to minimize background contaminants into the reactor due to permeation or leaks. The primary light source consists of a 200 KW argon arc lamp with specially designed UV filters that give a UV and visible spectrum similar to sunlight. Banks of blacklights are also present to serve as a backup light source for experiments where blacklight irradiation is sufficient, but these will probably not be used for the experiments discussed in this proposal that are designed to simulate ambient conditions. The interior of the enclosure is covered with reflective aluminum panels in order to maximize the available light intensity and to attain sufficient light uniformity, which is estimated to be ±10% or better in the portion of the enclosure where the reactors are located (Carter, 2002a). The reactors are attached to a semi-flexible moveable framework that allows the reactors to be emptied between experiments and reduces the volume under positive pressure control to prevent dilution due to sampling or leaks during experiments. A high-volume mixing system with Teflon® pipes and Teflon-coated flanges is used to mix the reactors and to exchange reactants between the reactors to achieve equal concentrations when desired. A diagram of the enclosure and reactors is shown on Figure 2

An AADCO air purification system that provides dry purified air at flow rates up to 1500 liters min⁻¹ is used to supply the air to flush the enclosure and to flush and fill the reactors between experiments. The air is further purified by passing it through cartridges filled with Purafil® and heated

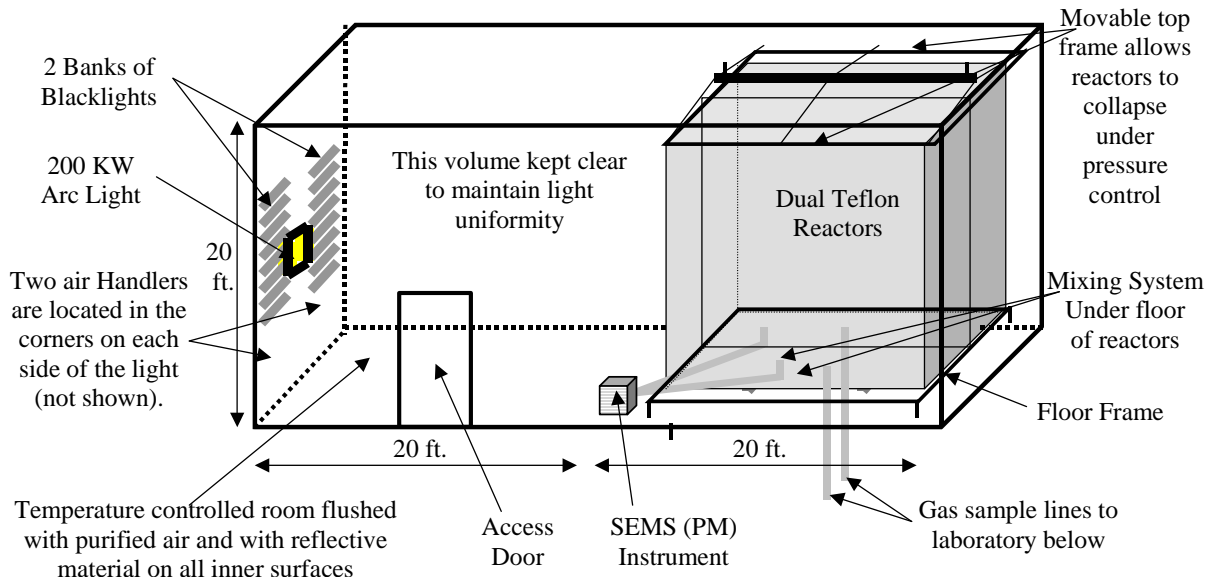


Figure 2. Schematic of the UCR EPA environmental chamber reactors and enclosure.

Carulite 300® which is a Hopcalite® type catalyst and also through a filter to remove particulate matter. The measured NO_x , CO, and non-methane organic concentrations in the purified air were found to be less than the detection limits of the instrumentation employed.

The chamber enclosure is located on the second floor of a two-floor laboratory building that was designed and constructed specifically to house this facility (Carter et al, 2002a). Most of the analytical instrumentation (except for the PM instrumentation) is located on the ground floor beneath the chamber, with sampling lines leading down as indicated on Figure 2.

Table 4 gives a list of the analytical and characterization equipment that is available for use with this project. Note that not all the instrumentation may be used for all the experiments, but most of the instrumentation listed there will be used, and experiments will not be carried out or will be repeated if instrumentation considered critical for characterization or mechanism evaluation is not available or is found to give invalid data.

Experiments to be Carried Out

For each of the pesticide or model compounds chosen for study, we will carry out “incremental reactivity” experiments for at least two different sets of conditions. Incremental reactivity experiments consist of simultaneously irradiating a base case ambient reactive organic gas (ROG) and NO_x mixture designed to be a simplified representative of ambient chemical conditions responsible for ground ozone formation, and irradiation of the same mixture with the test compound added. The ROG surrogate - NO_x base case experiments are expected to be the same as we are currently using for our coatings reactivity study (Carter, 2004c), and are as follows:

Table 4. List of analytical and characterization instrumentation for the UCR EPA chamber.

Type	Model or Description	Species	Sensitivity	Comments
Ozone Analyzer	Dasibi Model 1003-AH. UV absorption analysis. Also, a Monitor Labs Chemiluminescence Ozone Analyzer Model 8410 was used as a backup.	O ₃	2 ppb	Standard monitoring instrument.
NO - NO _y Analyzer	Teco Model 42 C with external converter. Chemiluminescent analysis for NO, NO _y by catalytic conversion.	NO NO _y	1 ppb 1 ppb	Useful for NO and initial NO ₂ monitoring. Converter close-coupled to the reactors so the "NO _y " channel should include HNO ₃ as well as NO ₂ , PANs, organic nitrates, and other species converted to NO by the catalyst.
CO Analyzer	Dasibi Model 48C. Gas correlation IR analysis.	CO	50 ppb	Standard monitoring instrument
TDLAS #1	Purchased from Unisearch Inc. in 1995, but upgraded for this project. See Carter (2002). Data transmitted to DAC system using RS-232.	NO ₂ HNO ₃	0.5 ppb ~ 1 ppb	NO ₂ data from this instrument are considered to be interference-free. HNO ₃ data may not be available for all experiments for this project
TDLAS #2	Purchased from Unisearch Inc. for this project. See Carter (2002). Data transmitted to DAC system using RS-232.	HCHO H ₂ O ₂	~ 1 ppb ~2 ppb	Formaldehyde data from this instrument are considered to be interference-free. The sensitivity for H ₂ O ₂ is expected to be too low to be useful for experiments for this project
GC-FID #1	HP 5890 Series II GC with dual columns, loop injectors and FID detectors. Various megabore GC columns available. Controlled by computer interfaced to network.	VOCs	~10 ppbC	Presently equipped with: 30 m x 0.53 mm GS-Alumina column used for the analysis of light hydrocarbons such as ethylene, propylene, n-butane and trans-2-butene and 30 m x 0.53 mm DB-5 column used for the analysis of C ₅₊ alkanes and aromatics, such as toluene, n-octane and m-xylene. Loop injection suitable for low to medium volatility VOCs that are not too "sticky" to pass through valves.
GC-FID #2	HP 5890 Series II GC with dual columns and FID detectors, one with loop sampling and one set up for Tenax cartridge sampling. Various megabore GC columns available. Controlled by computer interfaced to network.	VOCs VOCs	~10 ppbC 1 ppbC	30 m x 0.53 mm GSQ column used during this period. Loop injection suitable for low to medium volatility VOCs that are not too "sticky". Not used as primary analysis for most of these experiments. Tenax cartridge sampling can be used for low volatility or moderately "sticky" VOCs that cannot go through GC valves but can go through GC columns. 30 m x 0.53 mm DB-1701 column is currently in use. Not used for experiments discussed in this report.

Table 4 (continued)

Type	Model or Description	Species	Sensitivity	Comments
Luminol GC	Developed and fabricated at CE-CERT based on work of Gaffney et al (1998). Uses GC to separate NO ₂ from PAN and other compounds and Luminol detection for NO ₂ or PAN. Data transmitted to the DAC system using RS-232.	NO ₂	~0.5 ppb	NO ₂ measurements were found to have interferences by O ₃ and perhaps other species and are not used for quantitative mechanism evaluation.
		PAN	~0.5 ppb	Reliability of measurement for PAN not fully evaluated. Calibration results indicate about a 30% uncertainty in the spans. However, interferences are less likely to be a problem than for NO ₂ .
Gas Calibrator	Model 146C Thermo Environmental Dynamic Gas Calibrator	N/A	N/A	Used for calibration of NO _x and other analyzers. Instrument acquired early in project and under continuous use.
Data Acquisition System	Windows PC with custom LabView software, 16 analog input, 40 I/O, 16 thermocouple, and 8 RS-232 channels.	N/A	N/A	Used to collect data from most monitoring instruments and control sampling solenoids. In-house LabView software was developed using software developed by Sonoma Technology for ARB for the Central California Air Quality Study as the starting point.
Temperature sensors	Various thermocouples, radiation shielded thermocouple housing	Temperature	~0.1 °C	Primary measurement is thermocouples inside reactor. However, comparison with temperature measurements in the sample line suggest that irradiative heating may bias these data high by ~2.5°C. See text.
Humidity Monitor	General Eastern HYGRO-M1 Dew Point Monitor	Humidity	Dew point range: -40 - 50°C	Instrument performing as expected, but dew point below the performance range for experiments discussed in this report.
Spectroradiometer	LiCor LI-1800 Spectroradiometer	300-850 nm Light Spectrum	Adequate	Resolution relatively low but adequate for this project. Used to obtain relative spectrum. Also gives an absolute intensity measurement on surface useful for assessing relative trends.
Spherical Irradiance Sensors	Biospherical QSL-2100 PAR Irradiance Sensor or related product. Responds to 400-700 nm light. Spectral response curve included.	Spherical Broadband Light Intensity	Adequate	Provides a measure of absolute intensity and light uniformity that is more directly related to photolysis rates than light intensity on surface. Gives more precise measurement of light intensity trends than NO ₂ actinometry, but is relatively sensitive to small changes in position.
Scanning Electrical Mobility Spectrometer (SEMS)	Similar to that described in Cocker et al. (2001)	Aerosol Number and Volume concentration	Adequate	Provides information on size distribution of aerosols in the 28-730 nm size range, which accounts for most of the aerosol mass formed in our experiments. Data can be used to assess effects of VOCs on secondary PM formation.

- The “Maximum Incremental Reactivity” (MIR) base case consists of initial NO_x and ROG surrogate concentrations of 30 ppb and 0.55 ppmC, respectively. The NO_x level is designed to be representative of those in polluted urban areas in California and is in the range recommended by the staff of the CARB for the coatings reactivity study (Dongmin Luo, ARB Research Division, personal communication). The ROG/NO_x ratio is calculated to yield the greatest sensitivity of O₃ formation to added VOC concentrations, i.e., to represent MIR conditions. This is considered to be appropriate for testing mechanism for MIR calculations.
- The Low NO_x, “½ Maximum Ozone Incremental Reactivity” (MOIR/2) base case consists of initial NO_x of 25 ppb and initial ROG surrogate of 1.1 ppmC. The NO_x level is similar to that employed in the MIR experiments and is in the range recommended by the CARB staff. The ROG/NO_x corresponds to half the NO_x levels that give maximum ozone concentrations at the given ROG level (i.e., twice the MOIR ROG/NO_x ratio). This represents relative NO_x conditions that are relatively low but still not so low that VOC reactivities are not relevant to control strategies. These experiments are more sensitive to effects of VOCs on NO_x levels than is the case for the MIR experiments, and thus provide a useful complement to the MIR experiments. They are also useful in that the current SAPRC-99 mechanism gives a better simulation of the base case than is the case for the MIR base case (Carter, 2004a,c), which permits a more unambiguous mechanism evaluation.

In both cases, the ROG surrogate is based on that as that employed in “full surrogate” experiments in previous studies (e.g., Carter, 2000a and references therein, Carter et al. 1995a, 1996, 1997a-d, 1999, 2000a,b). This is designed to have one actual compound for each model species used in lumped molecule mechanisms used in current airshed models [e.g., RADM2 (Stockwell et al, 1997) or lumped SAPRC-99 (Carter, 2000b), and originally consisted of n-butane, n-octane, ethene, propene, trans-2-butene, toluene, m-xylene and formaldehyde in relative levels based on measured ambient ROG mixtures (Carter et al, 1995a). Subsequently formaldehyde was removed from the surrogate because it greatly simplified the experiments and its removal was not calculated to have a measurable effect on measured reactivity results if the total ROG level was increased by 10%. However, formaldehyde may be included in the surrogate used in this study if necessary and feasible.

The effect of the VOC on ozone formation is determined by differences between the base case and added test compound experiments on NO oxidation and ozone formation, and its effect on radical levels is determined by rates of consumption of m-xylene in the ROG surrogate. (M-xylene is useful for determining effects of VOCs on OH radical levels because it is the most reactive compound in the base case surrogate that reacts only with OH radicals). Although this is not a product determination study, we will attempt to identify and monitor any products that appear on our GC systems, and if possible measure the rate of consumption of the test compound. If we are unable to quantitatively analyze the test compound in the gas phase, separate tests, using a total carbon analyzer, will be used to assess if we can quantitatively inject the compound into the gas phase, and thus calculate the initial gas-phase concentrations based on the amounts injected.

These two types of incremental reactivity experiments (with appropriate replicates and perhaps amounts of added test compound varied) should provide a reasonably good test of a mechanism’s ability to predict the effect of the compound on ozone formation and radical levels under chemical conditions reasonably representative of polluted atmospheres where ozone formation is a problem. However, other types of chamber experiments may be conducted if it is determined that they may provide useful mechanism evaluation data for the particular compound and if time and resources permit. For example, if it is found that the compound enhances radical levels in the incremental reactivity experiments then single compound - NO_x experiments may provide useful data for mechanism testing to complement the reactivity runs. (Single organic - NO_x runs are not useful for compounds that inhibit radical levels because

the reactivity in such runs is low and dominated by chamber effects.) If the OH radical or other important rate constants are not known and the compound can be quantitatively monitored in the gas phase we may conduct experiments specifically designed to determine these rate constants if time and resources permit.

Note that if the compound is consumed only by reaction with OH radicals, reacts sufficiently rapidly, and can be quantitatively monitored, then the OH radical rate constant can be determined relative to the known rate constant for m-xylene from the relative rates of consumption in the incremental reactivity experiments. This has been successfully employed in our previous experiments with Texanol® to determine the OH radical rate constants for the two Texanol® isomers (Carter, 2004c).

Before conducting environmental chamber experiments with the compounds, tests will be conducted to determine if we can quantitatively analyze and inject the compound into the gas phase for the experiments. Although procedures we have successfully employed in our coatings reactivity study (Carter, 2004c) for Texanol® and ethylene glycol may be satisfactory, we are investigating an alternative injection method that may take less time and involve less exposure of the concentrated low-volatility VOC to the injection lines. This involves placing a measured amount of the compound on a filter in a tube inserted directly into the reactor and flushing it with heated N₂. This will be tested using a total carbon analyzer to determine if all of the compound is introduced into the gas phase during the time period used for the injection. If complete injection of compound into the gas phase can be assured, then the initial concentration used when conducting model simulations of the experiment can be calculated from the amount injected and the volume of the chamber. This permits use of experiments with the compound for mechanism evaluation even if we cannot quantitatively and reliably analyze the compound in the gas phase.

Of course, we will attempt to carry out reliable analyses of the test compounds in the gas phase, because this will verify the amounts injected and provide data needed to evaluate the mechanism and derive rate constants (if applicable). The gas chromatographic systems listed on Table 4 will be available for this purpose. For the more volatile compounds the GC systems with the loop analysis would probably provide the most precise data. For low volatility compounds the system with the Tenax cartridge sampling method will be employed. This was found to give good data for the Texanol® isomers and, if the appropriate column is employed, the glycols. If problems are encountered we will investigate use of alternative GC columns. However, as indicated above if we find we can quantitatively inject the compound into the gas phase as indicated by total carbon analysis methods, then it should be possible to conduct useable mechanism evaluation experiments with the compound.

Although making quantitative assessments of the effects of the selected compounds on PM formation is beyond the scope of this study, we will measure PM formation during the course of the experiments using the SEMS instrument described on Table 4. The results can serve as a qualitative indication of the extent to which the compounds affect PM, and in particular indicate those that are clearly strong PM precursors, such as was found to be the case for benzyl alcohol (unpublished results from this laboratory). Because the gas-phase conditions during these experiments will be well characterized for modeling, the results of these experiments could potentially also be used to evaluate predictive models for secondary PM formation from these compounds, should separate funding for this purpose become available.

The budget for this project is based on a total of 25 dual-reactor environmental chamber experiments being carried out. This includes at least 5 experiments for each of the four selected VOCs or model compounds, and five characterization or other experiments. This is based on a fairly conservative estimate of productivity, and it is possible that we may be able to carry out more experiments within the available funds if things go well. If this is the case, or if it is determined that the mechanisms for particular compound can be adequately evaluated with a smaller number of runs, we may be able to carry

out experiments on additional compounds. If so, the choice of compounds will be determined in consultation with the ARB staff and others as discussed above.

Mechanism Development and Evaluation

For each compound studied, we will survey the available literature concerning the kinetics, mechanisms, and theories for the relevant reactions of the compound or related compounds, and use this as a basis for deriving initial mechanisms or mechanism options. Roger Atkinson has studied a number of related compounds and is highly knowledgeable of the literature, is willing to serve as a resource for discussion, and his input will be sought and utilized where appropriate. Estimation methods such as those incorporated in the SAPRC-99 mechanism estimation system (Carter, 2000a) or developed based on more recent literature will be employed where appropriate. If the information about the compound is extremely limited or the mechanism is expected to be so complex and uncertain that any attempt at explicit mechanisms would be mostly speculation (as has been the case for aromatic hydrocarbons until recently), then alternative parameterized mechanism that incorporate expected overall effects of the reactions will be developed.

The preliminary mechanisms for the compounds will be incorporated into either the SAPRC-99 mechanism or the updated version of the SAPRC mechanism being developed for the ARB under contract 03-318 (see Related Programs, below). If the compound contains chlorine atoms and is expected to release them when it reacts (as is expected to be the case for 1,3-dichloropropene), then the chlorine module for the mechanism, which is also being updated for ARB contract 03-318, will be incorporated.

The preliminary mechanisms for the compounds will be utilized to estimate the appropriate amount to add in the incremental reactivity experiments, and assess if additional experiments, such as single compound - NO_x irradiations, may be useful. The results of the experiments will then be used to test the mechanisms by conducting model simulations of the experiments to determine if the mechanisms can correctly predict the effects of the compounds on various measures of reactivity. These include O₃ formation, NO oxidation, OH radical levels (as determined by m-xylene consumption rates), consumption rate of the test compound (if reliable analytical methods are available), and formation of formaldehyde, PAN, HNO₃ and other monitored products. The mechanisms will be adjusted or modified as needed to give predictions that are consistent with the available data, while still being consistent with available literature data and chemical reasonableness.

If the available data and theories are not sufficient to narrow down the possibilities to a single mechanism, alternative mechanisms will be developed that are consistent with the data. These can then be used to assess the effects of the uncertainty as to which alternative is correct on ozone impact assessments, as discussed below.

As discussed elsewhere (Jeffries et al, 1992; Carter and Lurmann, Carter et al, 1995b) chamber effects can affect the results of model simulations of chamber data and it is important to have an appropriate chamber characterization model when using chamber data for mechanism evaluation. As discussed by Carter (2004a), the UCR EPA chamber to be used in this study has already been characterized for this purpose, and this will be used as a starting point. Appropriate characterization experiments will be conducted periodically during the course of this program to determine if the existing characterization model is still applicable, and the chamber effects model will be modified as needed.

The mechanisms for the volatile pesticide compounds that are already represented in the current mechanism will be examined and updated if appropriate. These include chloropicrin, MIBK, acrolein, glycerine, and propylene glycol. Chamber data for mechanism evaluation are available for all of these compounds except glycerine, and the updated mechanisms will be re-evaluated using these data and

uncertain portions adjusted if appropriate. Chlorine chemistry will be incorporated into the mechanisms where appropriate.

If methyl bromide is chosen for study, we will incorporate the existing bromine chemistry that was used in our previous studies of bromine compounds (Carter et al, 1997b, Carter and Tuazon, 2000) and update this chemistry as appropriate. However, problems were encountered in these previous studies in developing a bromine mechanism that was consistent with these data, and an extensive research effort on atmospheric bromine chemistry, which may be necessary to resolve these issues, is beyond the scope of this project. If necessary, parameterized representations of the bromine chemistry applicable to methyl bromide may be used to estimate approximate ranges of ozone impacts of methyl bromide that are indicated by the methyl bromide incremental reactivity data obtained in this project.

To the extent feasible given the scope of this project and available information, we will attempt to derive estimated mechanism of other pesticide compounds of interest to the CARB and the stakeholder groups, so at least approximate ozone impact estimates can be derived. Information obtained in this project will be used to derive estimated mechanisms of structurally similar compounds. We will discuss with the California ARB and Department of Pesticide Regulation staff and appropriate stakeholder groups whether the volatility of pesticides such as chlorpyrifos and thiobencarb are sufficient that ozone reactivities are relevant, and if so we will examine the available data to derive estimated mechanisms that can be used to estimate reasonable ranges of likely ozone impacts. However, in some cases it may be that only upper limit ozone impact estimates can be derived.

The final report for this project will include recommendations as to additional research most needed to reduce uncertainties in mechanisms for the selected pesticide compounds of interest.

Ozone Impact Assessments

The experimentally evaluated or updated or new estimated mechanisms developed for this project will be used to calculate the ozone reactivities of the pesticide compounds in the MIR, MOIR, EBIR, “base case” and other ozone reactivity scales using the scenarios and reactivity assessment methods we have developed previously (Carter, 1994a,b, 2000a). If alternative mechanisms or mechanisms with significant uncertainties are developed for particular compounds, then reactivities will be calculated using the alternative mechanism or varied within the uncertainty range to determine the corresponding uncertainty in the MIR or other reactivity scale. Recommendations will be made as to the “best estimate” and upper and lower limit reactivities for the compounds, and the reactivity estimates will be assigned uncertainty classifications such as those given in Table 2, above. Chlorine chemistry will be incorporated when calculating reactivities for chloropicrin, 1,3-dichloropropene, and other compounds for which this may be appropriate. Recommendations will be made on how to represent these compounds in airshed models.

REPORTING AND DELIVERABLES

Periodic reports will be submitted to the ARB giving brief summaries of the progress and status of the program, problems encountered, and anticipated future schedules. These reports will be approximately quarterly or as required by the ARB. Additional reports concerning specific elements of the project, such as documentation of methods for assessing reactivity and uncertainty, will also be produced where appropriate and if requested by the CARB. The CARB may distribute these reports to other agencies or their industry advisory groups and consultants, as they deem appropriate. At the end of the project, a draft final report will be prepared documenting the work carried out and discussing the conclusions and recommendations resulting from the program as a whole. The final report will be independent of the quarterly reports and will not contain citations to them, though it may make reference to additional reports concerning specific elements of the project. Final versions of the draft annual reports or final report will be submitted within 30 days following receipt of comments from the CARB.

Environmental chamber data obtained for this program will be added to the UCR environmental chamber database for mechanism evaluation, and documented and made available to modelers through the Internet as described by Carter et al. (1995a). Software, spreadsheets and documentation developed for this program will also be made available on the Internet.

The reactivity estimates and uncertainty classifications for the pesticide compounds for which reactivity estimates were derived in this work will be added to the reactivity tabulations for all compounds for which reactivities have been estimated, and made available to the ARB and the public on the SAPRC reactivity website, as is the case with the current reactivity scale (Carter, 2003).

SCHEDULE

The period of performance of this project is for one year starting March 1, 2005. We expect to be ready to carry out chamber experiments as soon as the funding is available. Early during this project, or perhaps even before it begins, we expect to have a meeting or teleconference with the California ARB and Department of Pesticide Regulation staff and appropriate stakeholder groups to select at least some of the compound to be studied, so we can begin the experiments. We propose the first experiments being with 1,3-dichloropropene, since this is expected to be easy to analyze and handle and we can readily estimate its likely range of reactivity for the purpose of determining how much to inject in the experiments. The next compound we propose to study is MITC, which is also expected to be relatively easy to analyze and handle, though some initial mechanism estimation work will be needed to estimate the appropriate amount to add in the first experiment. The other compounds to study (which we recommend include at least one of the thiocarbamates) can be determined later, though we would prefer to get agreement on at least some early in the project so we can begin work on testing analytical and injection methods.

The experimental work should be concluded within the first six months of the project unless there is a delay in getting consensus on which compound to study. The remaining period of the project will be used for mechanism development and evaluation, ozone reactivity assessment, and preparation of the final report and other deliverables.

BUDGET

The amount requested for this project as discussed in this proposal is approximately \$99,850. This is based on our current costs for carrying out at least 25 environmental chamber experiments, with the cost of developing analytical and handling methods being included with the cost of the experiments. The budget also covers the Principal Investigator's time required to plan, oversee, and analyze the experiments, and an additional 2.3 person-months of the Principal Investigator's time for mechanism development and reporting.

An itemized budget for this proposed project is given on Table 5. Justifications and discussions of the various budget items are given below.

Labor and Fringe Benefits. The University charges for labor based on percentage of full-time equivalent (FTE) worked per month. Actual number of working hours per month will vary. Dr. Carter will serve as Principal Investigator for the project. The University charges for benefits as a direct cost. Benefit rates are 17% for faculty, 22% for research staff and 1.3% for students during the academic year.

Equipment. The purchasing of equipment is not necessary on this project

Travel. Travel will be necessary for both the discussion and reporting portions of this project. \$520 has been budgeted for the PI to travel to Sacramento for reporting and project discussion. University cost guidelines, as well as any other travel restrictions imposed by the California Air Resources Board for this project, will be adhered to during travel.

Electronic Data Processing. Communications Worker Fee in the amount of \$170 is included in the "Supplies and Expense" category. Communications Worker Fee is a direct charge to the grant for data network costs and is assessed in accordance with the payroll distribution of all personnel paid on all grants and contracts.

Miscellaneous. Because CE-CERT is a permanent off-campus facility, federal regulations require us to account for facilities rental as a direct cost. Facilities rental is charged based on 20.9% of Modified Total Direct Costs (MTDC). MTDC consists of total direct costs minus equipment, facilities rental, graduate student partial fee remission/health insurance (included in benefits), and subcontracts over \$25,000.

Indirect Costs. This project was budgeted on the assumption that it will be undertaken under the existing interagency agreement between the California Air Resources Board and the University of California. The indirect cost rate for that agreement was 10% of Modified Total Direct Costs. The 10% indirect cost rate applies only if the ARB does not apply federal funds to this project. If federal funds are used, the standard indirect cost rate of 26% must be applied.

Table 5. Itemized budget for proposed project.

	<u>Months</u>	<u>People</u>	<u>Time</u>	<u>Rate</u>	<u>Amount</u>	<u>Rate</u>	<u>Amount</u>	<u>Total</u>
William P. L. Carter	12.0	1	21%	\$8,950 /mo.	\$22,275	17.0%	\$3,787	\$26,062
QA Manager	12.0	1	1%	\$6,088 /mo.	\$609	22.0%	\$134	\$742
Laboratory Manager	12.0	1	2%	\$9,584 /mo.	\$1,888	22.0%	\$415	\$2,304
Maintenance Tech	12.0	1	3%	\$4,646 /mo.	\$1,732	22.0%	\$381	\$2,114
Sr. Instrument Tech	12.0	1	13%	\$5,330 /mo.	\$7,994	22.0%	\$1,759	\$9,753
Instrument Operator	12.0	1	3%	\$5,270 /mo.	\$2,108	22.0%	\$464	\$2,572
Chromatographer	12.0	1	17%	\$4,331 /mo.	\$8,792	22.0%	\$1,934	\$10,726
Postdoctoral Research Assoc.	12.0	1	5%	\$2,750 /mo.	\$1,650	22.0%	\$363	\$2,013
Students	12.0	1	8%	\$1,300 /mo.	\$1,300	1.3%	\$17	\$1,317
TOTAL PERSONNEL					\$48,348		\$9,254	\$57,602
SUPPLIES & EXPENSES								
Miscellaneous Laboratory supplies							4,058	
Maintenace Contracts							2,435	
Lamp Supplies							3,247	
TDLAS Supplies							1,623	
General Analyzer Repairs and Supplies							1,623	
Chamber Infrastructure Maintenance							3,247	
FEP Teflon							1,623	
Miscellaneous Office supplies							130	
Communication Worker Fee			<u>Hours</u>	<u>Rate</u>	<u>Amount</u>		170	
Staff/faculty			7.7	\$20.75 /hr,	160			
Students			1.0	\$10.375 /hr,	10			
TOTAL SUPPLIES & EXPENSES								\$18,157
TRAVEL								
Two trips to Sacramento to discuss project or present results							520	
TOTAL TRAVEL								\$520
TOTAL DIRECT COSTS SUBJECT TO OVERHEAD								\$76,279
EQUIPMENT								
NONE								\$0
OTHER								
FACILITY CHARGE					76,279			\$15,942
TOTAL DIRECT COSTS								\$92,222
INDIRECT COSTS								
10.0%					76,279			\$7,628
TOTAL COST								\$99,850

RELATED PROGRAMS

The objectives and current status of the other ongoing or proposed projects at our laboratories that are relevant to this proposal are summarized below. The ARB and SCAQMD coatings projects are relevant to this program because the experimental and modeling methods to be used are similar, and data will be obtained concerning the hydrocarbon constituents of pesticide VOCs listed in Table 3. The ARB mechanism development project is relevant because the updated mechanism will be used with the mechanisms developed for the specific pesticide VOCs as discussed above, and will include the updated chlorine mechanism that is needed for the chlorine-containing pesticide compounds. The EPA project is relevant because it provides general support for use of the UCR EPA chamber for ozone and PM mechanism development, and work on that project is expected to benefit the specific objectives of this proposal.

Evaluation of Atmospheric Impacts of Selected Coatings VOC Emissions

California Air Resources Board Contract Number 00-333

The College of Engineering Center for Environmental Research and Technology (CE-CERT) is nearing completion of a three-year experimental and methods and model development program aimed at reducing the uncertainties in estimating the impacts of architectural coatings emissions on photochemical ozone formation and other measures of air quality. The objectives and current status is as follows.

- Conducting environmental chamber experiments on at least 6 different representative petroleum distillates. After discussions with the ARB staff and the Coatings and other industry representatives on the CARB's Reactivity Research Advisory Committee (RRAC), the materials chosen for study are VMP Naphtha, ASTM types IA, IB, IC, and IIC1, and Aromatics 100. The chamber experiments with all these materials have been carried out and the results are now being analyzed.
- Conducting environmental chamber experiments on the important water-based constituent Texanol®, which is a registered trade name for a mixture of 2,2,4-trimethyl-1,3-pentanediol isobutyrate isomers. The chamber experiments were carried out and used to evaluate the current mechanism and the OH radical rate constants were also derived from the results of the experiments. The current estimated mechanism was found to be reasonably consistent with the data and the measured rate constants.
- Further development of the direct reactivity assessment method developed previously by Carter et al. (2002) for application to coatings constituents. Problems were encountered that could not be fully resolved within the level of effort available to this project, and we were unable to utilize this method to obtain useful data for this project.
- Develop and evaluate systematic procedures to quantify reactivities and compositional reactivity uncertainties of petroleum distillates using any given reactivity scale. A reactivity analysis of new compositional data obtained from Censullo et al (2002) was found to be generally consistent with the CARB's MIR "binning" method.

The final report for this project is currently under preparation and is expected to be submitted for review by January, 2005.

Environmental Chamber Studies of VOC species in Architectural Coatings and Mobil Source Emissions

California South Coast Air Quality Management District Contract 03468

This project provides additional funding to CE-CERT to support the objectives of the California ARB architectural coatings project discussed above and to conduct additional experiments regarding impacts of VOCs on ground-level ozone and particulate matter (PM). The specific objectives and current status are as follows:

- Conduct environmental chamber for reactivity assessment and chemical mechanism evaluation for at additional coatings VOCs selected by the SCAQMD in conjunction with discussions with the investigators and RRAC. The selected VOCs were ethylene and propylene glycols, benzyl alcohol, and butyl carbitol. The experiments with these compounds have been completed and the results are now being analyzed.
- Conduct measurements of PM formation in reactivity assessment and mechanism evaluation experiments not only for this project but also for the CARB coatings reactivity project. The results of these experiments can then be used to evaluate the PM formation potentials of the types of VOCs studied, and be available for developing and evaluating models for their impacts on PM formation in the atmosphere. The experiments for these projects have been completed and PM data are available for most of these. The results are now being analyzed.
- Conduct environmental chamber experiments with reactive organic gas (ROG) surrogates representing current ambient emissions and concentrations in order to determine the most appropriate set of “base case” experiments to use in incremental reactivity assessment experiments for this and the CARB architectural coatings reactivity project. After discussion with SCAQMD and CARB staff it was decided to base the surrogate on ambient air quality data to be provided by the staff. However, the data were not forthcoming in the time frame needed, it was decided to use the resources allocated to this task to conduct additional experiments to support the other tasks for this project.
- Evaluate the potential utility of the UCR EPA environmental chamber system for testing models for availability of emitted VOCs to react in the atmosphere to form O₃ and secondary PM. This work will be carried out in consultation with the atmospheric availability subgroup of the Reactivity Research Working Group (RRWG). After discussion with members of this group, it was determined to conduct experiments to assess whether there are interactions between ethylene and propylene glycol and seed aerosols injected into the chamber. No evidence for such interaction was found.

After discussion with the project officers for the two respective projects, it was agreed that the reporting for the two projects be combined. As indicated above, the final report for the combined projects is expected to be submitted for review by January, 2005.

Updated Chemical Mechanisms for Airshed Model Applications

California Air Resources Board Contract Number 03-318

The overall objective of this project is to develop and comprehensively evaluate updated detailed and condensed mechanisms for use in photochemical airshed models for predicting formation of secondary gas-phase and PM pollutants. The mechanisms should incorporate the most recent laboratory and environmental chamber data, improve representations for aromatics and PM precursors, and reduce uncertainties in estimated mechanisms for species where no data are available. Specific objectives include the following:

- Update the detailed SAPRC-99 mechanism and mechanism generation system to be consistent with the most recent data, theoretical assessments and estimation methods, and review and as appropriate revise the assumptions, approximations, and lumping approaches incorporated in the mechanism to optimize it for predictions of PM precursors and toxics as well as ozone reactivity.

- Improve the representation of the aromatics in the mechanism so its predictions are consistent with available current environmental chamber data and so it incorporates most recent laboratory results.
- Carry out environmental chamber experiments most needed to develop, evaluate, and reduce uncertainties in the updated gas-phase mechanism. Although carrying out experiments solely for PM mechanism evaluation is beyond the scope of this project, PM data will be collected during the experiments so the data should also be useful for PM mechanism evaluation as well.
- Develop and evaluate systematic procedures for deriving condensed mechanisms from the more detailed mechanisms developed for this project, with the goal of deriving a mechanism with computational efficiency comparable to that of CB4, but with the scientific basis of the more detailed mechanism.
- Develop an up-to-date capability of representing chlorine chemistry in the mechanisms developed for this project, including the reactions of chlorine atoms with the VOC species as well as the inorganic reactions.
- Incorporate the updated mechanisms into an appropriate selected regional model, and conduct simulations to test the implementation and to compare predictions of the same model and other mechanisms.

The results of this will provide the CARB, other regulatory agencies, and researchers with improved and more up-to-date models for gas-phase prediction. Although uncertainties and approximations will no doubt remain, this project should provide a basis for reducing uncertainties in future mechanisms, and establish standards and procedures for future mechanism updates.

Work on this project is now underway. The first effort is to develop an improved aromatics mechanism, and a new more explicit mechanism for selected aromatics is being developed and evaluated against available data. Difficulties are being encountered in simulating the available aromatics data and this effort is continuing. Environmental chamber experiments relevant to this aromatic mechanism development effort are also being carried out.

Utilization of a Next-Generation Environmental Chamber Facility for Chemical Mechanism and VOC Reactivity Evaluation

United States Environmental Protection Agency Cooperative Agreement No. X-83166601-0

The complexity and uncertainties in the atmospheric reactions that form secondary pollutants such as O₃ and PM requires that models that predict their formation be tested using environmental chamber data. However, the chambers and data used to develop the existing models have major limitations that results in uncertainties in models used for control strategy assessment. To address the need for improved model evaluation data, Congress appropriated \$2.9 million through the EPA for UCR to develop a “next generation” chamber facility to simulate atmospheric processes under more controlled and realistic conditions than previously possible. CE-CERT was chosen for this because of its leadership in environmental chamber research. The construction and initial characterization was completed in early 2003, and ozone and PM characterization and model evaluation experiments are underway. Results to date indicate that the new chamber meets its design goals and has already shown that there are problems with the mechanisms used in the current models. Additional information is available at <http://www.cert.ucr.edu/~carter/epacham>.

The current research agenda for the new chamber includes the following:

- Determine whether current models correctly predict secondary pollution formation from various the full range of conditions used in atmospheric models.
- Evaluate model predictions of effects of temperature and humidity on formation of O₃, PM, and other secondary pollutants from various types of VOCs.
- Investigate gas-phase and aerosol-phase interactions, including effects of aerosols on gas-phase processes and vice-versa.
- Obtain the highly characterized gas- and aerosol-phase data needed to develop and evaluate models for formation of secondary PM.
- Provide a platform to test and compare ambient monitoring equipment under controlled conditions where the air mass being monitored is well characterized.

The initial funding was sufficient to complete construction and characterize the chamber for experiments at a single temperature and dry conditions. Work to begin to more fully exploit the ability of the chamber to provide needed high-quality gas-phase and PM mechanism evaluation data under a range of temperature and humidity conditions has begun under EPA FY-03 funding, with the focus being characterizing and utilizing the chamber for PM research. We will utilize this additional available EPA funding to conduct this work, which is needed to obtain the full value from this unique new facility.

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BIOGRAPHICAL SKETCH

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Education

University of California, Riverside	Chemistry	B.A., 1967
California Institute of Technology	Chemistry	
University of Iowa, Iowa City	Physical Chemistry	Ph.D., 1973

Appointments

1973-present. University of California, Riverside, Air Pollution Research Center and College of Engineering Center for Environmental Research and Technology (joint appointment since 1992). Postgraduate Research Chemist 1973-1976. Assistant Research Chemist 1976-1981. Associate Research Chemist 1981-1987. Research Chemist 1987-present.

1970-73. University of Iowa. Graduate Research Assistant. Graduate teaching assistant, 1970-72.

1967-69. Graduate Research Assistant, California Institute of Technology.

Research Summary

Develops chemical mechanisms for urban and regional airshed models used for research and regulatory applications. Develops methods for evaluating relative ozone impacts of volatile organic compounds (VOCs) in the atmosphere. Develops VOC reactivity scales used in regulatory applications. Develops procedures for using environmental chamber data for evaluating such mechanisms and VOC reactivity assessment. Directs environmental chamber research programs. Participates in or directs kinetic or mechanistic studies related to photochemical smog formation.

Selected Recent Publications and Reports

W. P. L. Carter (2004). Evaluation of Gas-Phase Atmospheric Reaction Mechanisms for Low NO_x Conditions. Final Report to the California Air Resources Board, May 5.

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Honors

University of California, Riverside Non-Senate Distinguished Researcher Award, 1992.

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