Assessment of the Ozone and Aerosol Formation Potentials (Reactivities) of Organic Compounds over the Eastern United States

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Disclaimer

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Abstract

A direct sensitivity analysis technique is used for three-dimensional reactivity assessment (with respect to ozone formation) in eastern United States. Spatially and temporally resolved absolute and relative reactivities of 31 explicit and 9 lumped organic compounds and CO are calculated for two basecase and two future emissions scenarios. In order to be able to compare different species, the emissions of all the targeted organic compounds are perturbed equally on a mass basis. This perturbation followed the same spatial distribution as the total anthropogenic VOC emissions. Despite the variability (both spatial and temporal) in the absolute reactivities, relative reactivities were fairly constant. Different types of domain-wide reactivity metrics were considered. All the three-dimensional metrics showed a high level of inter-species consistency among them and had fairly low day-to-day variability. Domain-wide metrics were comparable with box model scales, but showed a less dynamic inter-species behavior. The evaluated metrics showed good level of consistency for different episodes, scenarios, and domains.

Executive Summary

Volatile Organic Compounds (VOCs) are one of the main ingredients in the formation of ozone and other photochemical oxidants. However, different organic compounds behave differently in the atmosphere, and have different oxidant formation potentials. As a result, state of California in some of its emission control regulations, considers both the mass emission rate and ozone formation potential (i.e., reactivity) of organic compounds.

Reactivity is defined as the amount of ozone produced from a unit mass of any specific organic compound added to the reacting mixture. Reactivity scales were originally developed using box model calculations. These calculations are usually carried out for conditions that lead to maximum ozone concentration or maximum species reactivity, resulting in Maximum Ozone Incremental Reactivity (MOIR) and Maximum Incremental Reactivity (MIR), respectively. The box model simulations, although valuable in describing the chemical mechanics of the system, lack the ability to accurately incorporate the physical phenomena (e.g., meteorology, transport, real world emission distributions, etc.) in the calculations. The objective of this research is to include these important variables in reactivity assessment through three-dimensional modeling coupled with the state-of-the-science sensitivity analysis techniques.

Reactivity modeling for this research was conducted using the Urban-to-Regional Multiscale (URM) model and over eastern US. Two basecase multi-day episodes in May and July of 1995, and two corresponding future episodes (May and July 2010) with reduced emissions are simulated. The model was updated to include SAPRC-99 chemical mechanism which is best suited for reactivity assessment. The mechanism included 42 explicit species, and reactivity assessment was carried out for 32 explicit and 9 lumped organics. The model was equipped with Decoupled Direct Method (DDM) for sensitivity analysis.

For reactivity calculations, the emissions of all organic compounds were perturbed equally (on a mass basis) and based on the real temporal and spatial distribution of anthropogenic VOC emissions. Absolute reactivities that were calculated by this method of perturbation showed a great deal of spatial and temporal variability. Relative reactivities of organics compounds were then estimated by normalizing the absolute reactivities to a base mixture. MOIR-3D, and MIR-3D metrics (corresponding to daily maximum ozone and maximum base mixture reactivity, respectively) as well as a least square metric (a linear fit for the cells with high ozone concentration and sizeable base mixture reactivity) for one and eight hour averaging time were calculated.

In general, reactivity metrics behaved consistently among different episodes. Major findings can be summarized as:

1. MOIR-3D was not shown to be a robust scale, as the chemical conditions at the location of the peak ozone could be very different from the box model MOIR conditions.

2. MIR-3D scales showed the best agreement with box model scales for all episodes.

3. The worst agreement with box model scales was seen for July 95 episode, which because of its high (mainly biogenic) VOC emissions, is the least radical limited.

4. The episodes with different emission scenarios (basecase and future) showed very high correlation in the estimated relative reactivity metrics.

5. Episodes with different meteorology (May and July), also showed fairly consistent behavior.

6. Most interestingly, a good correlation existed between the eastern US reactivity results, and the results from a similar study for central California.

7. Least square metrics for most of the species had a very good coefficient of determination (R^2), showing spatial consistency over the domain.

8. 1-hour and 8-hour metrics behave very similarly for most species.

9. The reactivity of aldehydes were consistently lower than the box model prediction.

In general, these results support the use of reactivity-adjusted emissions regulations.

1. Introduction

Tropospheric ozone is a secondary pollutant whose precursors are oxides of nitrogen (NO_x) and Volatile Organic Compounds (VOCs). Consequently, all ozone control measures rely on reducing emissions of one, or both, of these precursor classes. VOC controls are traditionally based on the total mass of organic compounds, not taking into account the unique characteristics of each individual species. However, individual VOCs behave differently in the atmosphere, and have differing ozone formation potentials. Therefore the concept of organic reactivity has been introduced to quantify the relative importance of organic compounds in producing ozone.

While a variety of reactivity measures have been proposed, they are usually developed using box model calculations. The physics of the atmosphere (i.e. meteorology), as well as spatial variability in precursor emissions and concentrations are not reflected in conventional box model calculations. Therefore, the applicability of reactivity scales in predicting atmospheric response to VOC control has been a controversial subject with significant policy implications. Three-dimensional air quality models (AQMs), on the other hand, incorporate physical details into their calculations and consider temporal/spatial variability of different species, and are considered to provide more realistic estimates of organic reactivities. Different investigators have used airshed models for reactivity estimation (e.g., McNair et al., 1992, Russell et al., 1995, Bergin et al., 1995). These studies have been mostly, although not solely (Khan et al., 1999, Hakami et al. 2002), limited to urban modeling and/or brute-force calculations. In this paper, three-dimensional organic reactivities for a regional domain are developed using a direct sensitivity technique.

2. Methodology

The Incremental Reactivity (IR) of an organic compound is defined as the amount of ozone produced per unit mass of VOC added to an organic mixture, or:

$$IR_i = \frac{\Delta O_3}{\Delta VOC_i} \qquad \text{(Equation1)}$$

The Maximum Incremental Reactivity (MIR) (Carter, 1994) is the primary reactivity scale used in several VOC control regulations such as the California Low Emission Vehicle/Clean Fuels Regulations and Aerosol Coating Regulations, and is developed using a 10-hr box model of daytime photochemistry. The MIR is calculated by adjusting NO_x emissions to yield the maximum IR for a given VOC mixture. MIR conditions are likely to occur in VOC-limited urban air mass, where the mixture is most sensitive to organic compounds because of low VOC-to-NO_x ratios. MIR conditions are of high practical significance because they represent areas of dense human population where ozone exposure is highest. Another box model reactivity scale, Maximum Ozone Incremental Reactivity (MOIR), is calculated by adjusting NO_x emissions to yield the peak ozone concentration for a given VOC mixture. MOIR conditions are likely to happen at higher VOC-to-NO_x ratios than MIR, more typical of aged urban air masses. Theoretically, reactivity scales can be derived as instantaneous values, but in practice they are usually reported as 1-hr averages. In light of the proposed 8-hour ozone standard, 8-hour reactivity scales have also been developed (Carter, 2000b).

Reactivities by definition are the sensitivity of ozone concentration to the mass of individual organic compounds added to the system, and therefore, different sensitivity analysis techniques can be applied for their assessment. In the context of three-dimensional modeling, reactivity scales can be written as:

$$MIR_{3D_i} = \max\left(\frac{\partial C_{O_3}}{\partial E_{VOC_i}}\right) \qquad \text{(Equation 2)}$$

and,

$$MOIR_{3D_i} = \left.\frac{\partial C_{O_3}}{\partial E_{VOC_i}}\right|_{\max(O_3)} \qquad \text{(Equation 3)}$$

where C_{O_3} is the ozone concentration in ppm, and E_{VOC_i} is the mass emission of each individual VOC. MIR_{3D_i}, and $MOIR_{3D_i}$ are the three-dimensional 1-hr averages of maximum incremental reactivity and maximum ozone incremental reactivity of organic compound *i*, respectively.

Box model reactivity scales are traditionally calculated by a brute-force approach where the response of ozone to a change in the initial amount of an individual VOC is estimated

at the end of a 10-hr simulation. Three-dimensional reactivities have also been estimated by this method, i.e. one-at-a-time perturbation of VOC emissions. The brute-force method is straightforward and easy to implement for few VOCs, but as the number of VOCs increases, the method becomes cumbersome and computationally expensive. More importantly, in the brute-force method a large perturbation can change the original characteristics of the mixture, while a small perturbation may result in numerical noise. Disadvantages of the brute-force approach can be avoided by using a direct method, where sensitivity equations are derived from model equations and solved. One such technique is the Decoupled Direct Method (DDM) which integrates sensitivity equations decoupled from concentrations (Dunker, 1981 and 1984). AQMs usually follow the time evolution of pollutants by solving the Atmospheric Diffusion Equation (ADE):

$$\frac{\partial C_i}{\partial t} = -\nabla(\mathbf{u}C_i) + \nabla(\mathbf{K}\nabla C_i) + R_i + E_i \qquad \text{(Equation 4)}$$

where **u** is the three-dimensional wind field, and **K** is the turbulent diffusivity tensor. *C*, *E*, and *R* are the grid cell average concentration, emission rate, and chemical reaction rate of species *i*, respectively. The corresponding sensitivity equation can be derived by differentiating ADE with respect to the emissions of VOC_j (Yang et al., 1997):

$$\frac{\partial S_{ij}}{\partial t} = -\nabla(\mathbf{u}S_{ij}) + \nabla(\mathbf{K}\nabla S_{ij}) + \mathbf{J}\mathbf{S}_j + E_j\delta_{ij} \qquad \text{(Equation 5)}$$

where S_{ij} is the sensitivity of species *i* to the semi-normalized emission of species *j* (in this case a VOC). $\mathbf{S}_j$ is the row vector of sensitivity coefficients, **J** is the Jacobian matrix ($J_{ik} = \partial R_i/\partial C_k$) of the reaction rates, and δ_{ij} is the Kronecker delta function. Equation 5 is structurally similar to the ADE and can be integrated (for the most part) by the same numerical integration routines, maintaining the structure of the AQM. DDM sensitivity (reactivity) calculations can be carried out for a large number of VOCs in an efficient manner, and computational overhead for additional VOCs is minimal. It is important to note that unlike concentrations, sensitivity equations, when decoupled from concentrations, are linear with respect to sensitivity coefficients and can be solved accordingly.

2.1. Model Description

The Urban-to-Regional Mulitscale (URM) model is used here to simulate atm spheric behavior and the effects of emissions from three major source types. The URM-1ATM is a three-dimensional, Eulerian photochemical air quality model that accounts for gas and aerosol phase chem itation processes (Boylan et al., 2002). The URM-1ATM also incorporates the DDM sensitivity analysis to calculate the local derivatives of specified model outputs simultaneously with concentration calculations. The multiscale approach with a direct sensitivity calculation method is used to capture the dynamic physics and chemistry while reducing the computational load. The multiscale grid desi for this project is shown in Figure 1. Multiscale gridding differs

from nested gridding in that the different sized grids are not calculated independently, but as one continuous domain. The finest horizontal scale gridding has 24km cells, and the other grid cell sizes are 48km, 96km, and 192km. The finest grid is placed over major source regions such as the Ohio River Valley, where many power plants and large industries are located, and over highly populated regions such as the east coast corridor. This scheme captures high population-related sources such as automobile exhaust, fast food restaurants, etc. The vertical model grid has 7 nonuniform layers, with the thinnest layer near the ground and the layers thickening with an increase in altitude. This vertical scheme allows detailed treatment of ground level sources and best represents ground level mixing and dry deposition processes, allowing for diurnal changes in mixing depths, and captures aloft multi-day transport events.

Gas phase chemistry is updated to the SAPRC-99 chemical mechanism (Carter, 2000a) with 42 explicit VOCs, considered as the most suitable chemical mechanism for reactivity assessment (RSAC, 1999). No emissions were assigned to the newly added explicit VOCs (compared to the base mechanism), as they were only perturbed in the sensitivity field. In other words the concentration calculations remain unaffected by the addition of the new explicit VOCs. Table 1 gives a summary of URM-1ATM model. Note that URM has aerosol simulation modules, but those were not updated to the SAPRC-99 mechanism, and therefore were not used in this study. However, Very few of the species assessed have secondary products as discussed later. Table 2 shows a list of 40 organic species and CO that are considered for reactivity assessment and explicitly expressed in the mechanism. MIR and MOIR reactivity scales from box model calculations (for both 1-hr and 8-hour averaging periods) are also shown for these species (Carter, 2000b).

The URM was applied to four simulation episodes, May 22-27 and July 10-18, 1995, and May 22-27 and July 10-18, 2010. The two “basecase” 1995 episodes are used to ensure adequate model performance by comparing ambient measurements with simulated concentrations. The two future case episodes are used for evaluation of potential control strategies under anticipated ambient conditions, and their effect on organic reactivities. Here, the comparison between 1995 and 2010 also measures the response of reactivity metrics to emissions changes. The two base episodes, May 1995 and July 1995, were selected because high quality and quantity data were available, they were both previously modeled using a different multiscale grid definition but with the same simulation system (Boylan et al., 2002), and because combined they represent significant meteorological variation. The July episode represents polluted ozone season period and the May episode represents a cooler, more average air quality period. Excluding model “ramp up” days, 5 and 8 days of simulation results are available for May and July episodes, respectively.

2.2. Model Inputs

Spatially and temporally detailed air quality fields, meteorological properties, and emissions inputs specific to each simulation episode are required as inputs to the URM. Air quality information is used for initial conditions (ICs) and time-dependent boundary conditions (BCs). Ground level gas species IC/BCs are derived using data from the Aerometric Information Retrieval System (AIRS) (USEPA, 2001), the North American

Research Study on Tropospheric Ozone for the Northeast (NARSTO-NE) (Mueller, 1998), and other smaller measurement studies. The upper domains IC/BCs are set to free troposphere values (Seinfeld and Pandis, 1998) and linear interpolation is used to derive the IC/BC concentration changes with altitude.

Meteorological information is provided by an application of the Regional Atmospheric Modeling System (RAMS) (Pielke et al., 1992) in a nonhydrostatic mode, including cloud and rain microphysics. Three nested grids were used for simulations, which were then mapped to the URM multiscale grid. No horizontal interpolation was necessary, however the RAMS vertical structure has thirty-one layers so inputs were aggregated to the seven URM layers. The RAMS applications matched the URM horizontal domain extent and the upper boundary altitude (12,867 meters).

Gridded, hourly, day-specific emissions were generated using the Emissions Modeling System (EMS-95) (Wilkinson et al., 1994) for the four modeling episodes. Emissions from elevated point sources, such as power plants and large industries, are injected into the appropriate vertical layer using stack parameters such as temperature and velocity of emissions. Ground level sources are incorporated as boundary conditions, and include on-road and off-road mobile sources, biogenic sources, low-level point sources, and anthropogenic area sources. Foundation data for point, area, and on-road mobile emissions were developed by Pechan/Avanti (2001), and point source emissions estimates for major utilities in the domain were refined using utility-provided day specific data. EMS-95 applies MOBILE 5b (USEPA, 1994) for vehicle-dependent emissions factors of CO, NOx, and total organic gases. On-road mobile source emissions estimates incorporate data on vehicle miles traveled and vehicle mix by state, county, and roadway type; and speeds by vehicle and roadway type. Biogenic emissions were estimated using the U.S. EPA BEIS2 (Pierce and Geron, 1996; Pierce, 1996; Pierce et al., 1990) as a function of the RAMS temperature and solar radiation inputs. Mobile sources are also calculated as a function of temperature. Emissions are projected 15 years into the future from the 1995 meteorological episodes by accounting for growth in population and associated emissions and accounting for compliance with current and anticipated emissions regulations. This future case projection is referred to as 'on the way' and is described in more detail elsewhere (Odman et al., 2002). Table 3 presents the estimated average day emissions for the May and July basecases, and future episodes.

2.3. Reactivity Perturbation and Calculation

Absolute VOC reactivities are calculated by perturbing the emissions in the sensitivity field. This perturbation (E_j in equation 5) is done equally (on a mass basis) for all the VOCs, by a fraction (α) of the total VOC emissions. For each grid cell:

$$E_j = \alpha \sum_k E_k \qquad \text{(Equation 6)}$$

where index *k* indicates any VOC with anthropogenic emissions, and E_j is the emission perturbation for species *j* (in units of *gm VOC / cell – min*). The perturbation, unlike brute-force method, is insensitive to the numerical noise introduced from taking the

difference between two close values. Due to linearity of the sensitivity equations, the choice of perturbation fraction is arbitrary. In other words, since the reactivities are calculated on a relative basis (to each other), any magnitude of perturbation fraction can be applied, as long as it is done equally for all species. The perturbation is only applied to the sensitivity field, and due to the decoupled nature of the method, concentrations remain unchanged. This method is applied to ensure that three-dimensional reactivity estimation is based on the spatial and temporal emissions distribution of organic compounds identical to those used in concentration simulations. In addition, since all VOCs are perturbed equally (on a mass basis) their ozone formation potential can be readily compared. This method of perturbation produces the same effect as previous brute-force studies (e.g., Bergin et al., 1995), while avoiding the non-linearity problems that are encountered when changing the concentration field. For this study all VOCs were perturbed by two percent of the total anthropogenic VOC emissions, for each grid cell, and at each simulation hour.

2.4. Reactivity metrics

Carter's reactivity scales are given in units of *gm O_3 / gm VOC*; which are possible to derive since a box model is used. A similar value is not appropriate for three-dimensional reactivities because emissions from the whole domain are being perturbed, and concentrations all over (in three dimensions) are responding. Of interest, however, is how surface level ozone responds to domain-wide perturbations. For practical applications (i.e. development of ozone control strategies), it is the relative magnitude of individual reactivities, as opposed to their absolute values, that are meaningful. In other words, because of high degree of variability in the absolute reactivities, it is more insightful to know how reactive each organic compound is compared to the others. Therefore, three – dimensional Relative Incremental Reactivities (RIRs) are defined as:

$$RIR_i = \frac{IR_{3D_i}}{\overline{IR}_{Base}} \qquad \text{(Equation 7)}$$

where IR_{3D_i} is the absolute reactivity of species *i* (in units of *ppm O_3 / gm VOC*) calculated from three-dimensional modeling (S_{ij} in equation 5), and $\overline{IR}_{Base}$ is the normalized reactivity of a base VOC mixture:

$$\overline{IR}_{Base} = \sum_{j=1}^{N} y_j IR_j \qquad \text{(Equation 8)}$$

where N is the total number of VOCs in the mixture and y_i is the mole fraction (per mole of carbon of the base mixture) for each organic compound in the base mixture. The mixture composition is chosen (Carter, 2002) such that it represents typical anthropogenic organic emissions. The mixture composition is shown in Table 4 (Carter, 2002).

Unlike box model calculations, three-dimensional simulations result in a spatial distribution of reactivities. For practical applications, a metric (or metrics) should be chosen to represent an ensemble measure from spatial distributions in form of smaller subsets of values. These metrics can also be compared to the box model scales. In this study three types of metrics are examined. MIR-3D metric is defined as the 1-hr RIR of each species, at the time and location where the base mixture has its daily maximum reactivity. MOIR-3D is defined as the 1-hr RIR of each species at the time and location of the daily maximum ozone concentration. MIR-$3D_{8hr}$, and MOIR-$3D_{8hr}$ metrics are calculated in the same manner but for 8-hour averaging periods. A Least Square Relative Reactivity (LS-RR) (Carter, 2002, personal communication) is calculated as the slope of the line that represents the absolute reactivity of each species versus the reactivity of the base mixture. This metric is calculated for grid cells and times with ozone concentration and base mixture reactivity above a set threshold value, and from 1-hour or 8-hour average incremental reactivity values at the time of the maximum ozone concentration for each cell. While the MIR-3D and MOIR-3D metrics are calculated from the values for a single cell and averaging period (but selected from all the cells/times), LS-RR metric represents a larger number of cells/times that are of particular interest (high ozone concentration and/or significant base mixture reactivity).

3. Results and discussion

Figure 2 shows spatial distribution of ozone at the time of the peak, for the May and July basecase episodes. May episode is considerably lower in ozone concentration and is characterized by lower biogenic VOC emissions and temperatures. Ozone performance evaluation for both basecase episodes are shown in Figure 3. The ozone concentrations typically have low biases, and the normalized error is generally less than 25%.

Figures 4, and 5 show examples of spatial and temporal variability in absolute reactivities of few VOCs for July 1995 episode. The spatial plot is shown at the time of episode's maximum ozone concentration, and the time series are chosen to represent two different predominant chemical regimes, i.e. VOC-limited urban air mass (Chicago) and NO_x-limited area dominated by biogenic emissions (Great Smoky Mountains). Firgure 5 also shows spatial plots of relative reactivity for the same time. Finally, Figure 6 shows times series of relative reactivities for five major urban areas in the domain, where typically higher base mixture reactivity is seen.

Absolute reactivities show a great deal of temporal and spatial variability, which can only be captured in a physically meaningful way through a three-dimensional modeling approach. As can be seen from the plots, depending on the location, time, and species, absolute reactivities can span a range of orders of magnitude. Another interesting observation is that a compound can be less or more reactive compared to other VOCs, (e.g., formaldehyde and 2MBT). Since the perturbation of emissions in the sensitivity field follows the pattern of the total VOC emissions, high VOC reactivities are found in areas (or downwind of areas) where anthropogenic emissions of both VOC and NO_x are highest. Figure 5 also shows that organic reactivities, as expected, are considerably higher for VOC-limited air masses, where the peak ozone usually occurs. Comparing absolute and relative reactivities in Figure 4 (or the times series for Chicago in Figures 5 and 6), shows that normalizing absolute reactivity of species to a base mixture reduces the variability. Note that in Figure 6, the points with insignificant base mixture reactivity are set to zero. Among the five cities shown in Figure 6, only Chicago has significant negative base mixture reactivity at times, as it is the only city in the group that is usually not a recipient of major NO_x plumes from upwind sources.

Three-dimensional relative maximum incremental reactivity (MIR-3D), and maximum ozone incremental reactivity (MOIR-3D) metrics, as well as those of 8-hour moving averages ($MIR\text{-}3D_{8hr}$, and $MOIR\text{-}3D_{8hr}$) are evaluated using equations 7 and 8. 1-hour and 8-hour least square metrics are also calculated for an ozone concentration threshold of 80 ppb, and 60 ppb, respectively. As both May episodes and July 2010 have significantly lower ozone concentrations, the 1-hour threshold for those episodes was set to 60 ppb. In least square calculations, the cells with negligible anthropogenic emissions, and those with small base mixture reactivity (less than 0.1 ppb, about 1% of the maximum value for July 1995 episode) are excluded. Also, points with negative base mixture reactivity are excluded, as they can result in misleading metrics.

Figure 7 shows a comparison between box model MIR scales (relative to the base mixture) and MIR-3D and LS-RR scales for the July and May 1995. In general, 3D scales

show a less dynamic behavior over the species range, i.e. lower reactivity for more reactive species and vice versa. MIR-3D scales are closer to box model scales than the least square metric, as conditions in the maximum reactivity cell tends to be more similar to box model MIR conditions. Among all episodes, MIR-3D metric of the July 1995 episode shows the worst agreement with the box model scales, as it has the highest VOC emissions and is the least radical limited. It is important to note that aldehydes are consistently lower in relative reactivity than the box model prediction. In addition to the less radical limited condition than the box model represents, three-dimensional modeling also accounts for the carryover of the species that provide a source for radicals (e.g. photolysis of ozone, nitrous and nitric acid, hydrogen peroxide, etc.) into the next days. This sustained source of radicals into the following day makes the radical producing organics less reactive than box model. Other significant over-predictions by the box model scales include tri-methyl benzene (although xylenes generally show good agreement) and a-pinene, while methanol is somewhat under-prdeicted.

Figure 8 shows different 1-hour and 8-hour metrics for all episodes. A detailed summary of all reactivity scales for different episodes/scenarios is given in the tables of Appendix A. Given the significant temporal and spatial variability in absolute reactivities, the relative reactivity metrics are comparable from one episode to another. Additionally, the relative ranking of species remains similar on different scales. As mentioned before, May episodes have far less biogenics and are more radical-limited, resulting in higher reactivity for more reactive VOCs that are important sources of radicals. Least square metrics generally show a high coefficient of determination and low standard error of least square slope (relative reactivity) estimate (Appendix A) with the exception of benzaldehyde. MOIR-3D scales are the most variable and inconsistent among different scales (e.g., Figure 8-b), as the conditions at location and time of the maximum ozone concentration can be significantly different than the box model. In Figure 9, the ratio of absolute reactivity at the peak ozone location and time to the maximum reactivity for each species is plotted in comparison to the box model ratio for the May 1995 episode. It can be seen that some of the days have similar behavior to the box model, while other days are significantly different. It appears that MOIR-3D is not a robust metric for comparing the ozone formation potential of organic compounds.

In a previous study three-dimensional relative reactivity metrics were calculated for central California. For that study the same chemical mechanism (excluding acrolein, and dodecane) was implemented in a Multiscale Air Quality SImulation Platform (MAQSIP). Apart from applying different models, the methodology for reactivity assessment was identical to that of the current study, and therefore, a comparison of the results is insightful in better understanding the effects of different domains on reactivity metrics. Figure 10 compares 1-hour MIR-3D and LS-RR reactivity scales for July 95 episode, with those calculated for a different episode/domain in California. Considering the significant differences in the chemical regimes in these two domains, the scales show good agreement. A significantly larger than one slope, is mainly due to the highly reactive, radical producing VOCs being far more reactive in the more radical limited regime (central California in this case due to much lower biogenic emissions). The slope of the least square fit in Figure 10 (and other similar figures) is affected largely by more

reactive species, which are significantly (with the exception of ethene) more reactive in the more radical limited regime. In Figure 11 a very good correlation between May and July 1995 episodes, for both MIR-3D and LS-RR scales is seen. Slope larger than one are expected as May episodes are more radical limited (lower biogenic emissions). Figure 12 also shows good correlation between reactivity scales in different emissions scenarios. Again, larger-than-one slopes (especially for least square metrics) shows that with further emission control measures, the domain will become more sensitive to organic emissions, i.e. more radical limited. Note that the least square metrics are driven by grid cells that have higher base mixture reactivity, and those cells tend to be downwind urban areas that are mainly dominated by mobile and area source emissions, and therefore, less affected by aggressive NO_x control from power plants in future years. The very high R^2 for t

daily distinction can be seen for both May episodes. This results in higher R^2 for daily approach, while for the July episode such distinction does not exist, and therefore R^2 for the episodic metric is higher (as some days with fewer points can have much lower R^2).

In the original proposal, it was planned to look at the impact of the species on particulate matter formation, though in much less detail than ozone. The choice of organics for assessment includes only a few that have condensable products in the approach that is applied in URM at this time. The impact on non-organic particulate matter formation from incremental increases in emissions of these organics is small and varied temporally and spatially. Time did not permit extensive assessment of the particulate matter formation from the organics chosen. This is an area that is of significant importance, as noted in the recommendations.

4. Conclusions and Recommendations

Direct sensitivity calculation was shown to be effective for three-dimensional reactivity assessment. Absolute reactivities of different compounds were calculated by injecting equal amounts (on a mass basis) of each species into the sensitivity field. The perturbation followed the same spatial pattern as total anthropogenic VOC emissions. The absolute reactivity values for different organic species, or for the same species at different locations and times, can cover a range of few orders of magnitude.

Relative reactivity of each VOC was calculated with reference to a base mixture, and different domain-wide metrics were defined. The relative reactivities are consistent with each other, independent of which metric is chosen; MIR-3D, MOIR-3D, or LS-RR, and for different averaging periods. The metrics compare reasonably well (for most species) among different episodes, different emissions scenarios, different domains, and different averaging times. MOIR-3D, however, behaves erratically at some days where the base mixture has very small reactivity at the location of the daily peak. MIR-3D shows the best agreement with the box model, with a very high degree of correlation for most of the episodes. July 95 episode which is the least radical limited (because of high VOC emissions) is farthest from the box model scales. Least square reactivity scales have a high coefficient of determination and low standard error for most of the species. And finally, 3-D reactivities of aldehydes are consistently lower than the box model. The results suggest that relative reactivity scales present a fairly robust method for ranking organic species based on the their potential effect on ambient ozone concentration.

A study should also be conducted over the whole US, to look at the impact of using finer or coarser resolutions. The results here suggest that the use of reactivity scales is robust across domains, given the consistency found between this study, and similar ones conducted for southern and central California. On the other hand, the box model MIR scale appears to over-emphasize the differences between organic reactivities, particularly for the higher end of the spectrum and radical sources.

The species chosen for study in this first phase were based on their impact on ozone, and not particulate matter. Few of those produce condensable organic material, and their impact on non-organic aerosol formation is small. Given the importance of particulate matter, and that organic material is a substantial fraction of the PM, compounds leading to PM formation should be studied as well. This should be done using a modeling platform like CMAQ, which includes an advanced treatment of organic phase distribution and DDM-3D. Different scales may have to be developed for PM formation. A modeling system can be readily developed to rapidly quantify species “reactivities”. Such a system is superior to one based on box model representation because, as seen here, comprehensive models do differ from box model calculations for some important species. This would be particularly true for organic PM formation. The system cab designed to run on a personal computer, and take as input the necessary reaction(s) and reaction rate(s) for desired organic compounds.

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Table 1 URM-1ATM specifications

Chemistry	SAPRC-99
total number of species	109
steady state species	7
explicit VOCs	42
total number of reactions	252
number of photolytic reactions	31
chemical solver	hybrid (Young and Boris, 1977)
Horizontal Transport	finite element scheme
advection scheme	PPM (Colella and Woodward, 1984)
Emissions	processed using EMS-95
total number of emitted species	39

Table 2 Organic compounds and their absolute (Carter, 2000b) and relative (per mole-C) box model reactivity. Explicit species that are added to the base mechanism are highlighted.

		Absolute box model scales				Relative to base mixture			
Compound	**Code**	**MIR**	**MOIR**	**MIR_{8hr}**	**$MOIR_{8hr}$**	**MIR**	**MOIR**	**MIR_{8hr}**	**$MOIR_{8hr}$**
2-Methyl 2-butene	**2MBT**	14.450	4.650	9.610	7.040	4.734	4.125	5.869	6.26
1,3-Butadiene	**BUTD**	13.580	4.830	7.900	5.520	4.284	4.126	4.646	4.726
Propene	**PRPE**	11.580	4.430	6.500	4.570	3.798	3.934	3.973	4.067
Isoprene	**ISOP**	10.690	3.950	6.250	4.210	3.402	3.404	3.708	3.637
m-Xylene	**XYLM**	10.610	3.190	6.240	4.170	3.291	2.68	3.608	3.511
Ethylene	**ETHE**	9.080	3.700	4.770	3.560	2.981	3.289	2.919	3.172
Formaldehyde	**HCHO**	8.970	2.560	5.910	4.060	6.288	4.86	7.723	7.725
Acrolein	**ACRO**	7.61	2.78	4.15	2.56	3.355	3.319	3.41	3.063
1,2,4 Trimethyl benzene	**124B**	7.180	2.320	4.110	2.710	2.241	1.961	2.391	2.295
Acetaldehyde	**CCHO**	6.840	2.560	3.890	2.520	3.524	3.572	3.736	3.524
a-Pinene	**APIN**	4.290	1.560	2.580	1.780	1.365	1.344	1.531	1.538
p-Xylene	**XYLP**	4.250	1.360	2.200	1.450	1.318	1.142	1.272	1.221
Toluene	**TOLU**	3.970	1.170	2.000	1.310	1.221	0.9741	1.146	1.093
Methylcyclopentane	**MCPT**	2.420	1.330	1.140	0.870	0.7936	1.181	0.6968	0.7743
Ethanol	**ETOH**	1.690	0.930	0.770	0.610	0.9103	1.356	0.7731	0.8917
iso-Pentane	**IPNT**	1.670	1.020	0.790	0.670	0.5627	0.9307	0.4962	0.6127
n-Pentane	**N_C5**	1.540	0.960	0.710	0.600	0.5189	0.8759	0.446	0.5487
Methyl ethyl ketone	**MEK**	1.480	0.650	0.740	0.500	0.6234	0.7414	0.581	0.5716
2,2,4 Trimethyl pentane	**224P**	1.440	0.810	0.690	0.570	0.4804	0.7316	0.429	0.516
n-Butane	**N_C4**	1.330	0.830	0.610	0.520	0.4514	0.7628	0.3859	0.479
Acetylene	**C2H2**	1.250	0.490	0.590	0.430	0.3797	0.4031	0.3341	0.3545
n-Butyl acetate	**BACT**	0.890	0.540	0.410	0.330	0.4028	0.6617	0.3459	0.4053
Benzene	**C6H6**	0.820	0.340	0.370	0.270	0.2494	0.28	0.2098	0.2229
Methyl t-butyl ether	**MTBE**	0.780	0.470	0.380	0.340	0.3212	0.524	0.2916	0.3799
Methanol	**MEOH**	0.710	0.340	0.340	0.270	0.5309	0.6884	0.4739	0.548
Isopropanol	**IPOH**	0.710	0.390	0.370	0.320	0.3324	0.4944	0.3229	0.4066
Dodecane	**DODC**	0.66	0.43	0.26	0.16	0.2189	0.3861	0.1607	0.144
Acetone	**ACET**	0.430	0.170	0.220	0.140	0.1946	0.2083	0.1856	0.172
Ethane	**C2H6**	0.310	0.200	0.140	0.120	0.109	0.1905	0.09178	0.1145
Carbon monoxide	**CO**	0.060	0.040	0.030	0.030	0.03926	0.07087	0.03659	0.05327
Methane	**CH4**	0.010	0.010	0.010	0.010	0.003739	0.01012	0.006969	0.01015
Benzaldehyde	**BALD**	-0.610	-1.640	-0.550	-1.090	-0.2161	-1.573	-0.3631	-1.048
Higher aldehydes	**RCHO**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Alkanes	**ALK3**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Alkanes	**ALK4**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Alkanes	**ALK5**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Aromatics	**ARO1**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Aromatics	**ARO2**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Olefines	**OLE1**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Olefines	**OLE2**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Lumped Terpines	**TRP1**	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Table 3 Average daily domain-wide emissions for different episodes (tons per day).

	NO_x				VOC			
	Biogenics	Mobile	Point	Area	Biogenics	Mobile	Point	Area
July 1995	5100	21300	30200	3000	176200	20600	8800	18300
July 2010	5100	14700	15300	3300	176200	13500	6600	16000
May 1995	3000	19900	24600	5700	78400	17000	7900	19100
May 2010	3000	13200	14300	6000	78400	10700	6200	17300

Table 4 Composition of the base reactivity mixture (Carter, 2002).

species or group	moles/mole-C
C2H6	8.68e-3
ALK2[1]	7.16e-3
N_C4	1.50e-2
ALK4[2]	3.51e-2
ETHE	2.23e-2
OLE1	1.16e-2
2MBT	4.56e-3
BUTD	1.36e-3
ISOP	3.77e-4
APIN	7.23e-4
C6H6	7.25e-3
TOLU	1.29e-2
XYLM	7.04e-3
CRES[3]	8.92e-4
HCHO	9.86e-3
CCHO	2.16e-3
RCHO	1.68e-3
BALD	1.05e-3
ACET	4.66e-3
MEK	4.56e-3
INERT	7.77e-3
C2H2	5.30e-3
MEOH	9.09e-3
MTBE	5.07e-3
BACT	3.71e-2
ETOH	2.12e-2
ACRO	1.21e-3

1- ALK2 is 0.5 (C2H6 + N_C4)
2- ALK4 is 0.25 (MCPT + IPNT + N_C5 + 224P)
3- CRES is 0.5 (TOLU + BALD)

Table5a R-squared (top-right half) and slope (bottom-left half) for correlation between different MIR-3D metrics.

	July 1995	July 2010	May 1995	May 2010	CA	Box Model
July 1995		0.99	0.97	0.99	0.92	0.92
July 2010	1.15		0.98	0.98	0.95	0.94
May 1995	1.21	1.05		0.98	0.98	0.97
May 2010	1.16	1.00	0.95		0.95	0.95
CA	1.13	0.98	0.97	0.99		0.99
Box Model	1.21	1.05	1.01	1.04	1.03	

Table 5b R-squared (top-right half) and slope (bottom-left half) for correlation between different LS-RR metrics.

	July 1995	July 2010	May 1995	May 2010	CA	Box Model
July 1995		0.97	0.91	0.89	0.84	0.81
July 2010	1.18		0.97	0.95	0.86	0.84
May 1995	1.39	1.20		1.00	0.92	0.91
May 2010	1.44	1.25	1.04		0.91	0.91
CA	1.34	1.13	0.95	0.90		0.98
Box Model	1.59	1.35	1.14	1.08	1.16	

Table 5c R-squared (top-right half) and slope (bottom-left half) for correlation between different LS-RR metrics with a no-intercept model.

	July 1995	July 2010	May 1995	May 2010	CA	Box Model
July 1995		0.96	0.73	0.75	0.67	0.71
July 2010	1.25		0.77	0.87	0.67	0.70
May 1995	1.02	0.82		0.86	0.91	0.90
May 2010	1.29	1.09	1.16		0.72	0.67
CA	0.90	0.70	0.89	0.62		0.98
Box Model	1.32	1.03	1.06	0.77	1.16	

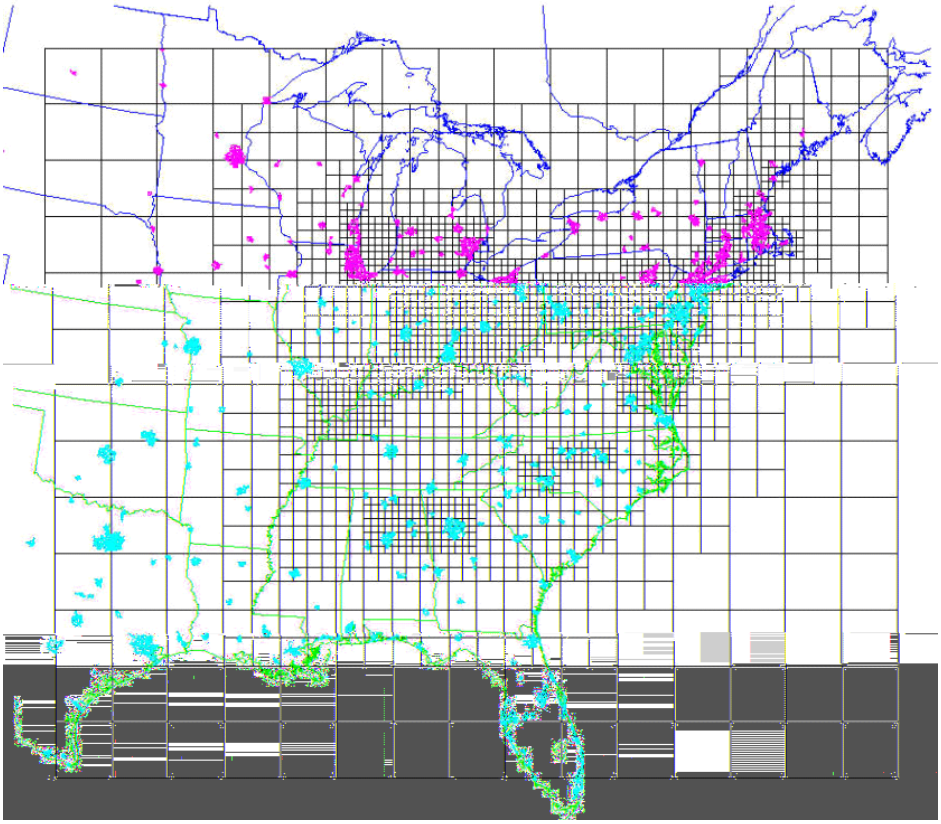


Figure 1 The multiscale grid designed for this study. The purple areas represent high population densities.

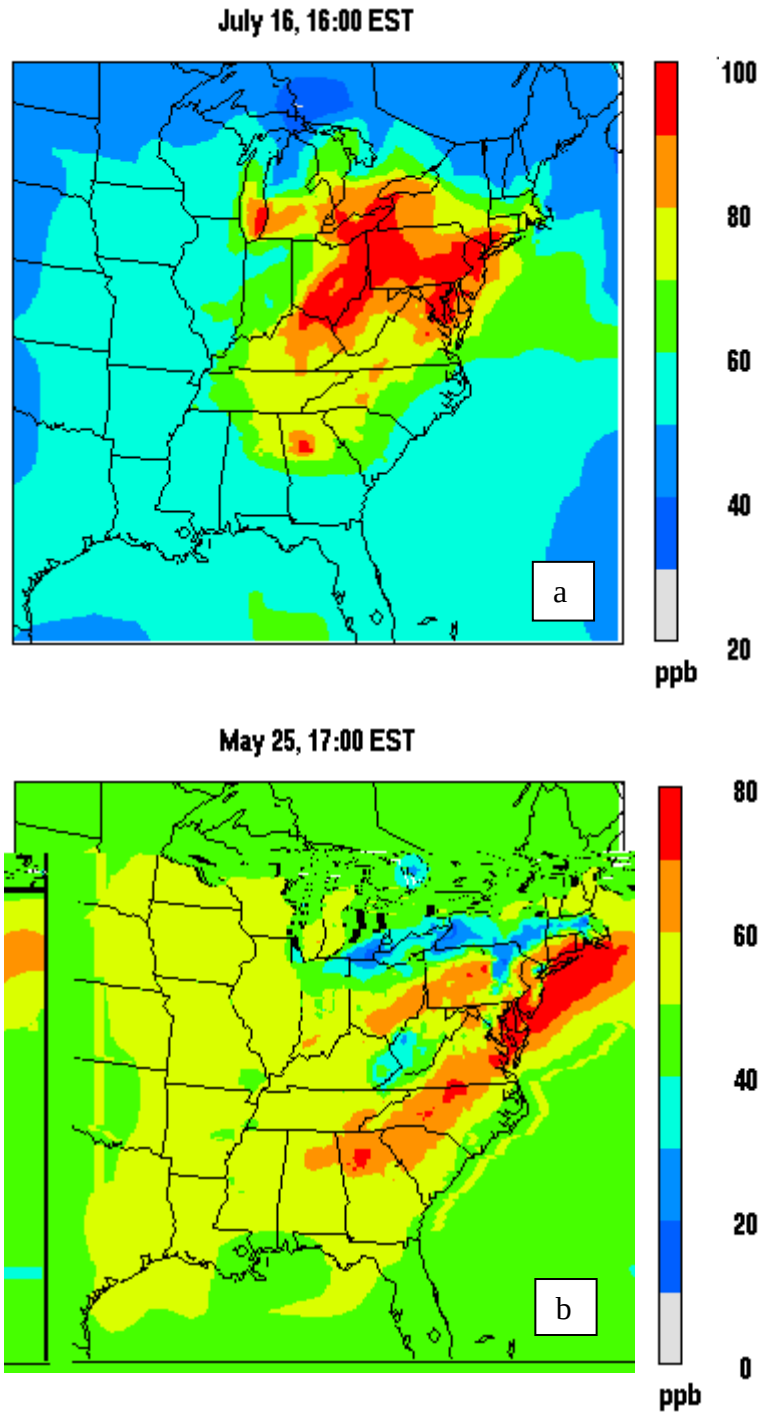


Figure 2 Ozone concentrations at the time of peak for a) July 1995, and b) May 1995.

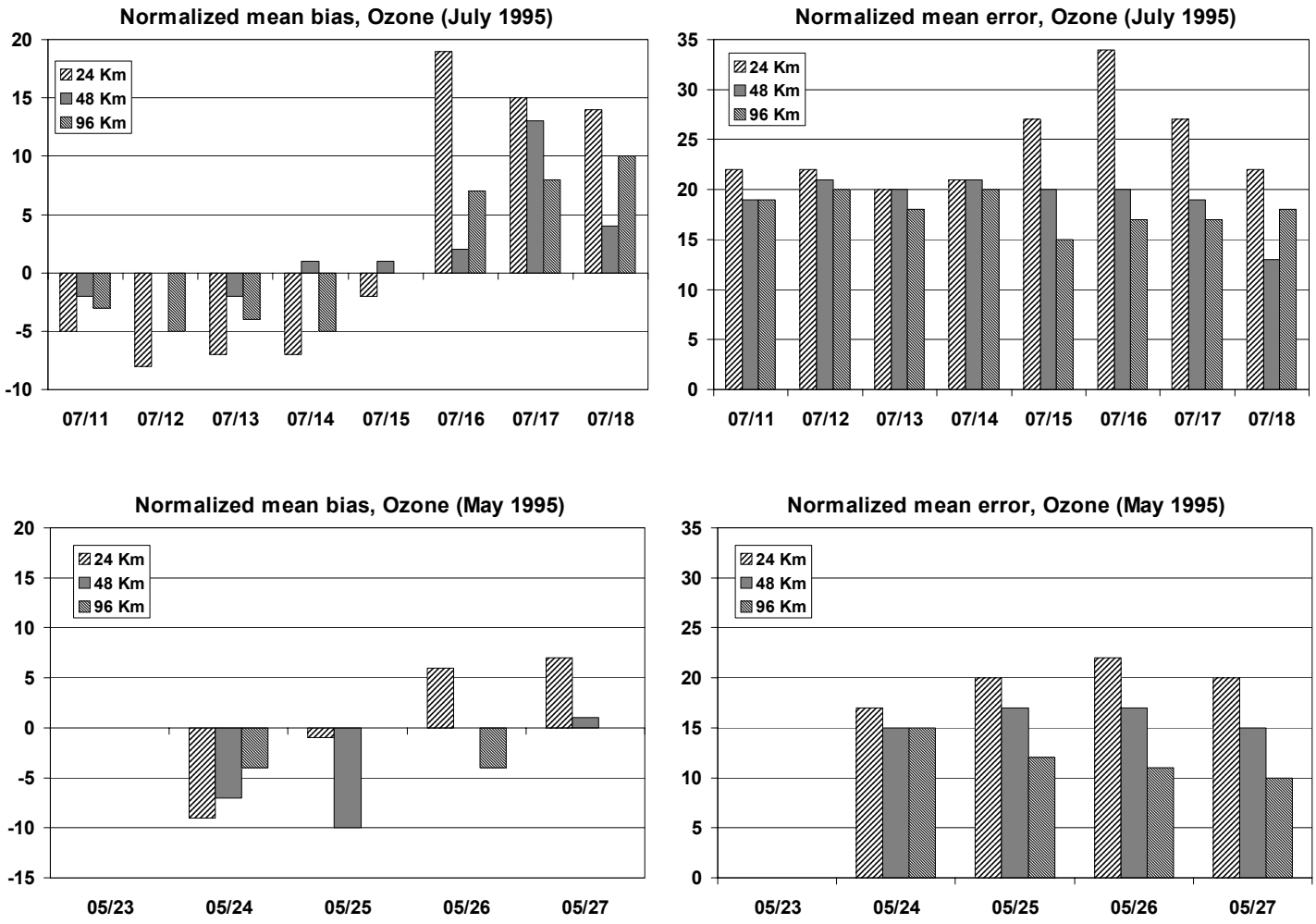


Figure 3 Ozone performance evaluation for the two basecase episodes and different grid resolutions.

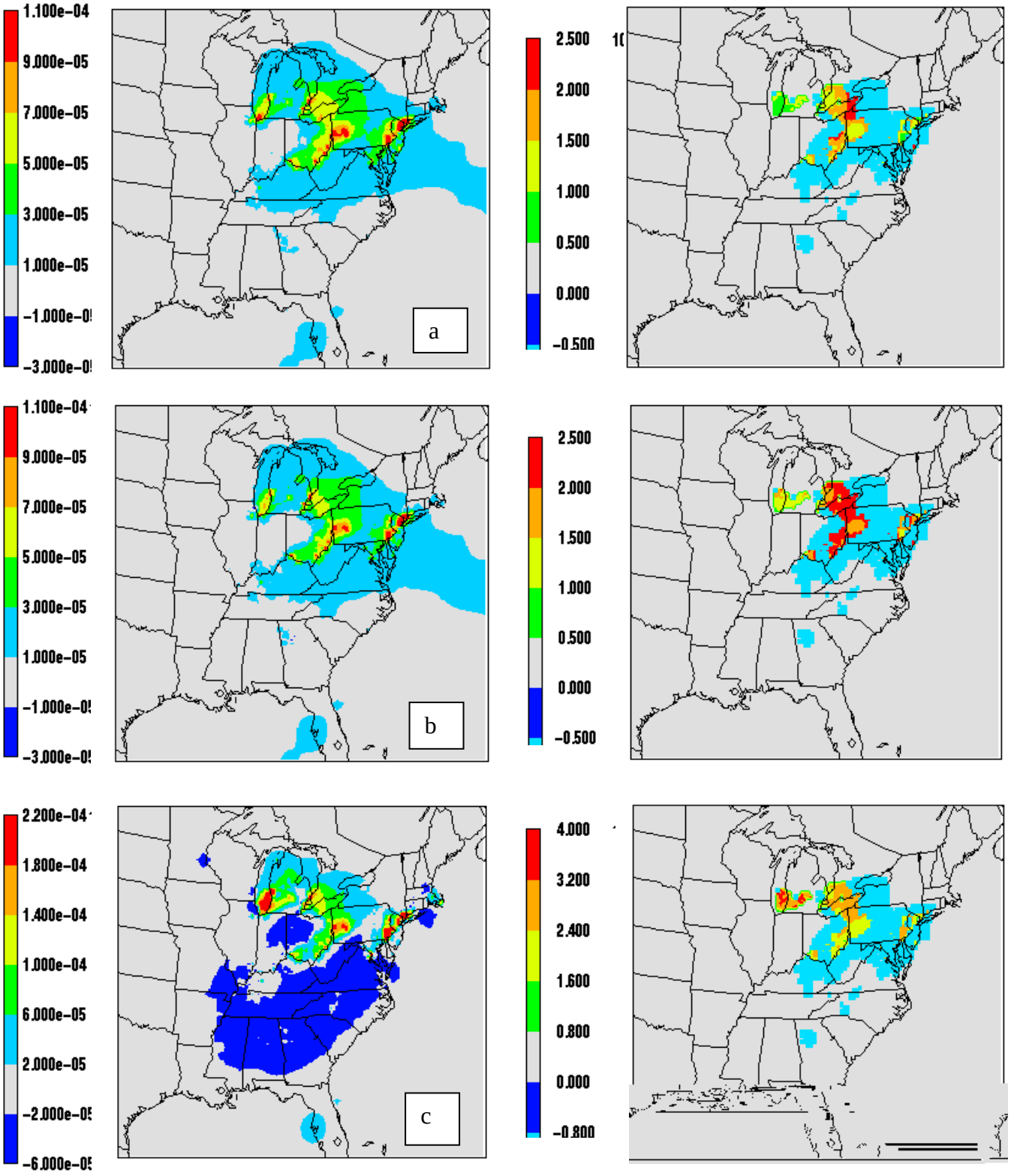


Figure 4 Sample of spatial distribution of absolute (left) and relative (right) reactivities for a) n-butane, b) ethanol, and c) isoprene. Light blue in the relative reactivity plots represents areas with insignificant base mixture reactivity.

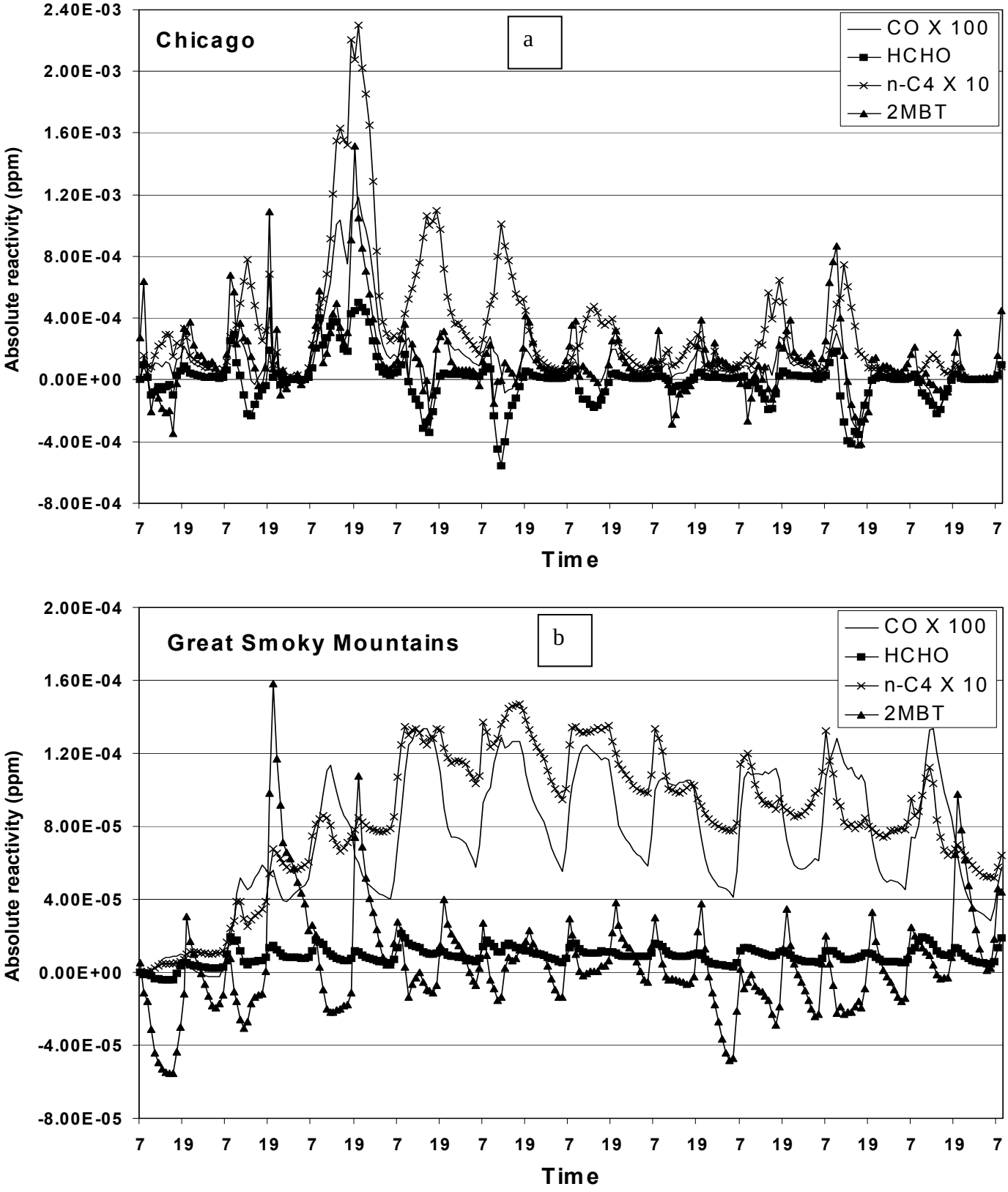
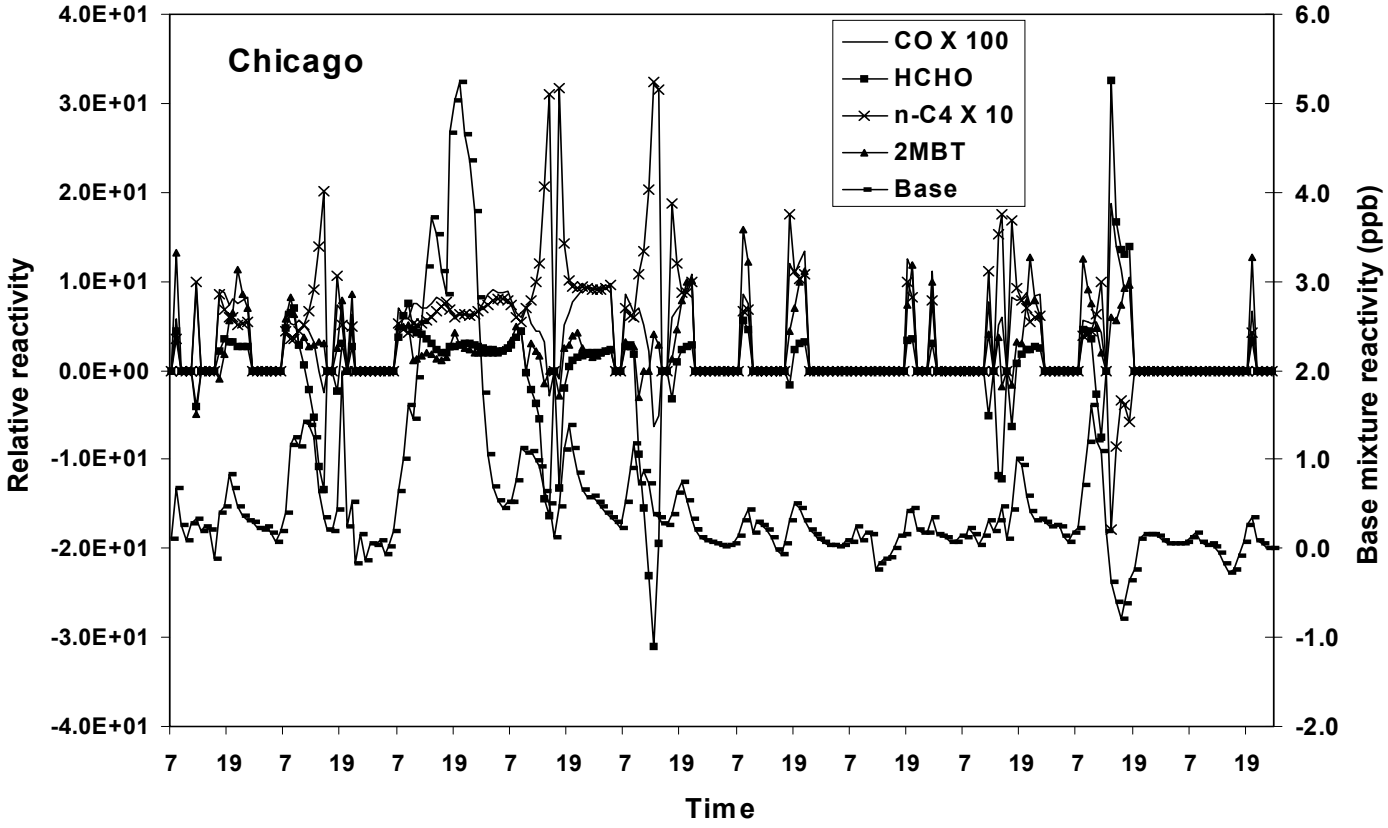
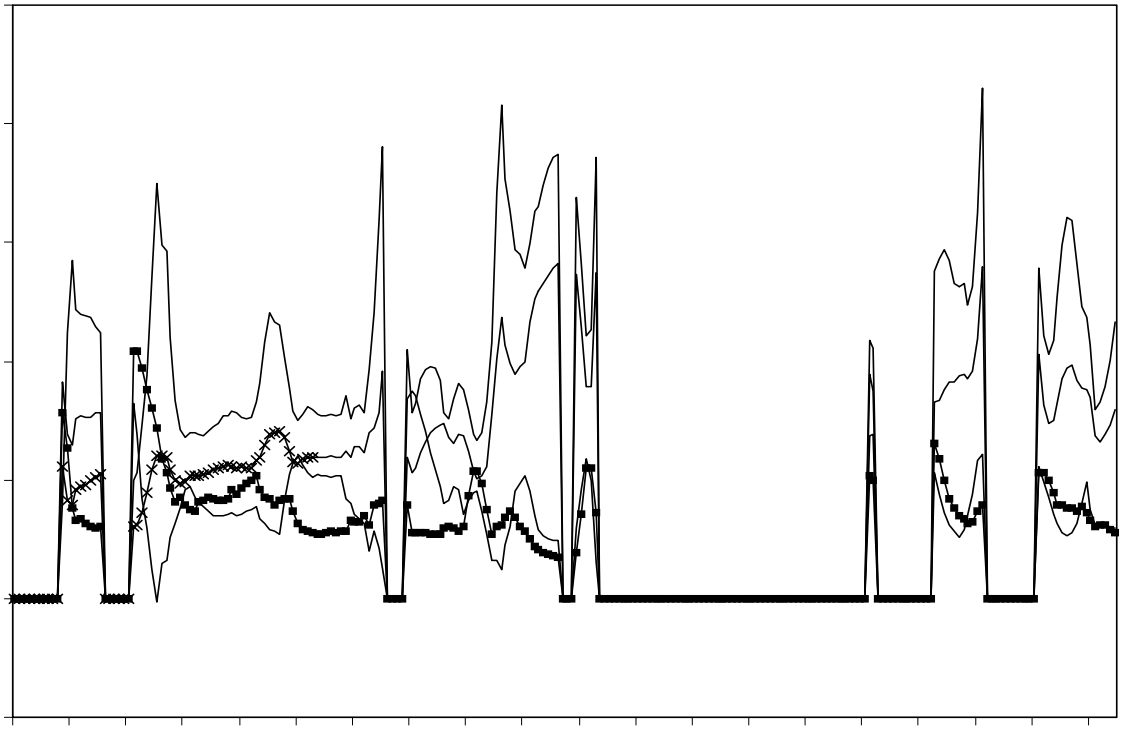
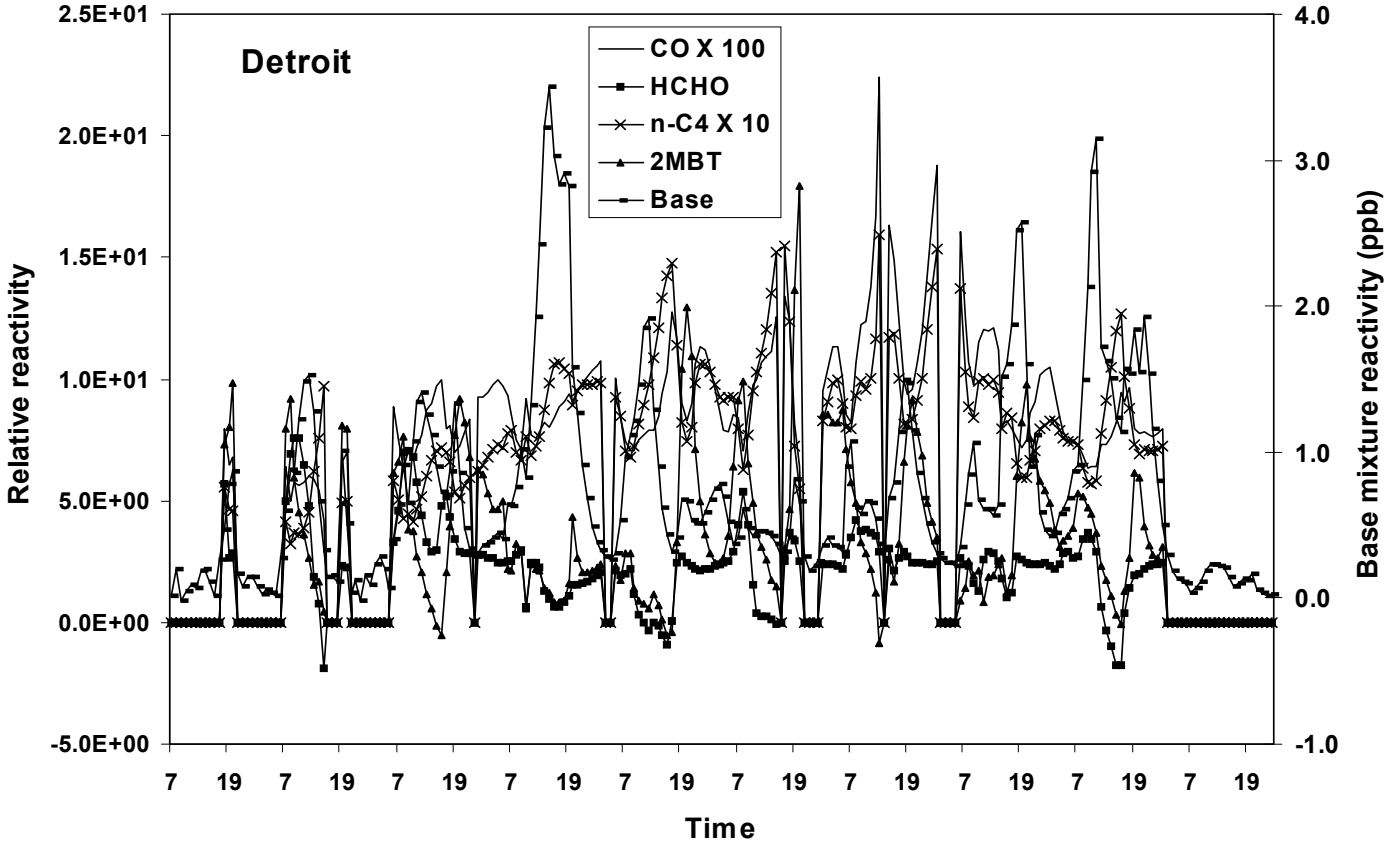


Figure 5 Samples of time series for select VOCs at a) Chicago, and b) GSM.


Chicago
CO X 100
HCHO
n-C4 X 10
2MBT
Base
Relative reactivity
Base mixture reactivity (ppb)
4.0E+01
3.0E+01
2.0E+01
1.0E+01
0.0E+00
-1.0E+01
-2.0E+01
-3.0E+01
-4.0E+01
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
7
19
Time




Detroit
CO X 100
HCHO
n-C4 X 10
2MBT
Base
Relative reactivity
Base mixture reactivity (ppb)
2.5E+01
2.0E+01
1.5E+01
1.0E+01
5.0E+00
0.0E+00
-5.0E+00
4.0
3.0
2.0
1.0
0.0
-1.0
7 19 7 19 7 19 7 19 7 19 7 19 7 19 7 19 7 19 7 19 7 19
Time

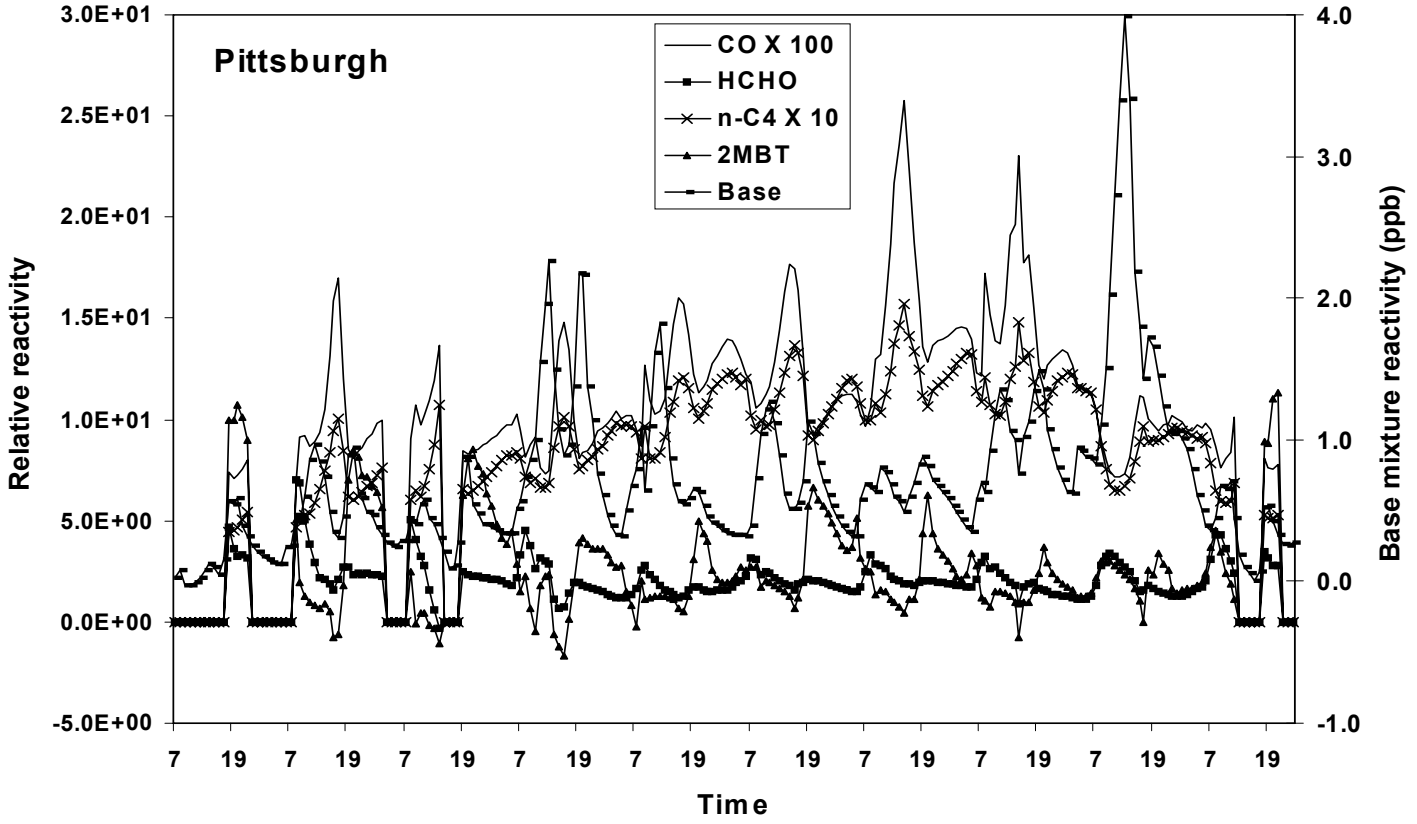
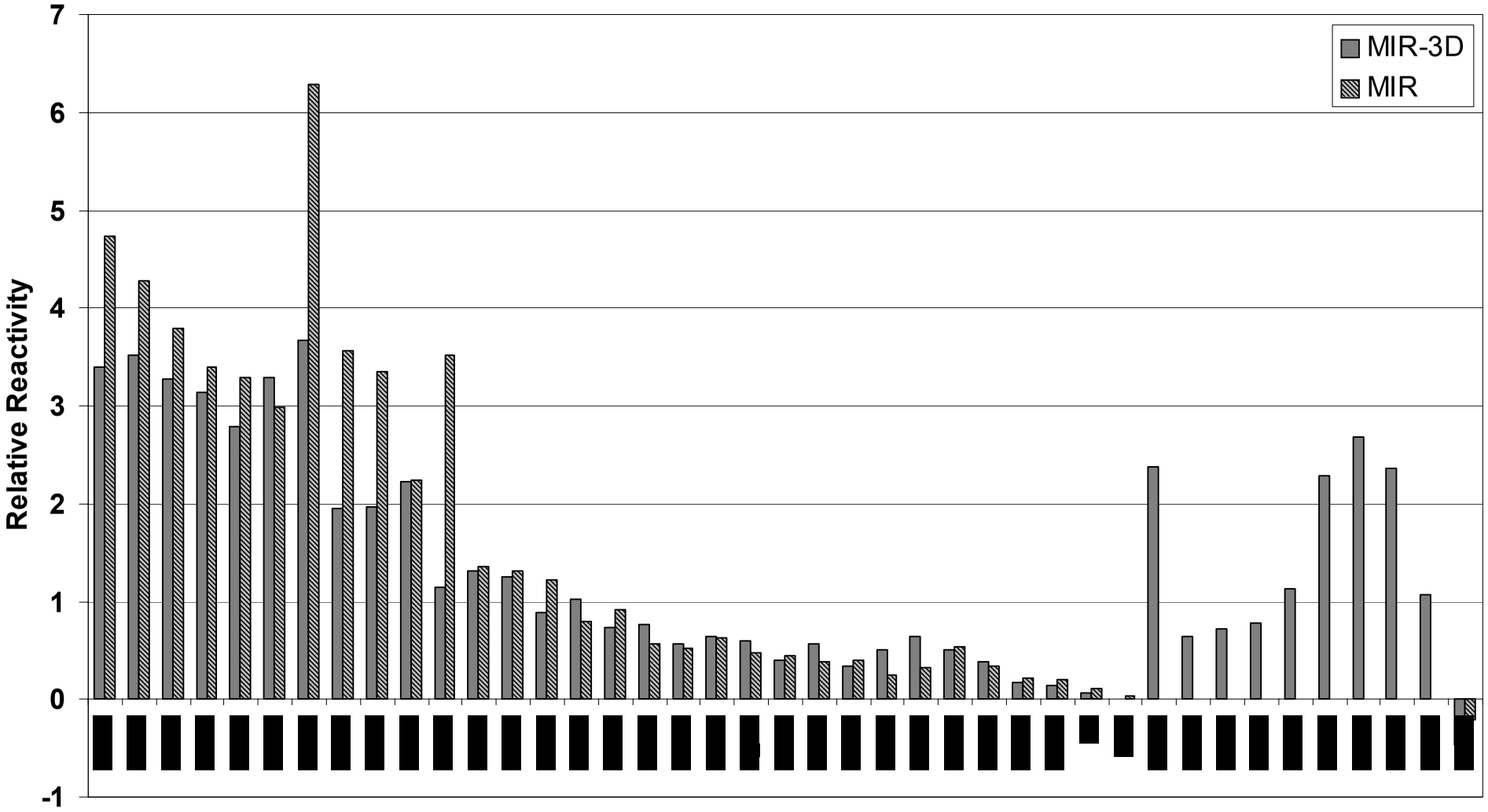
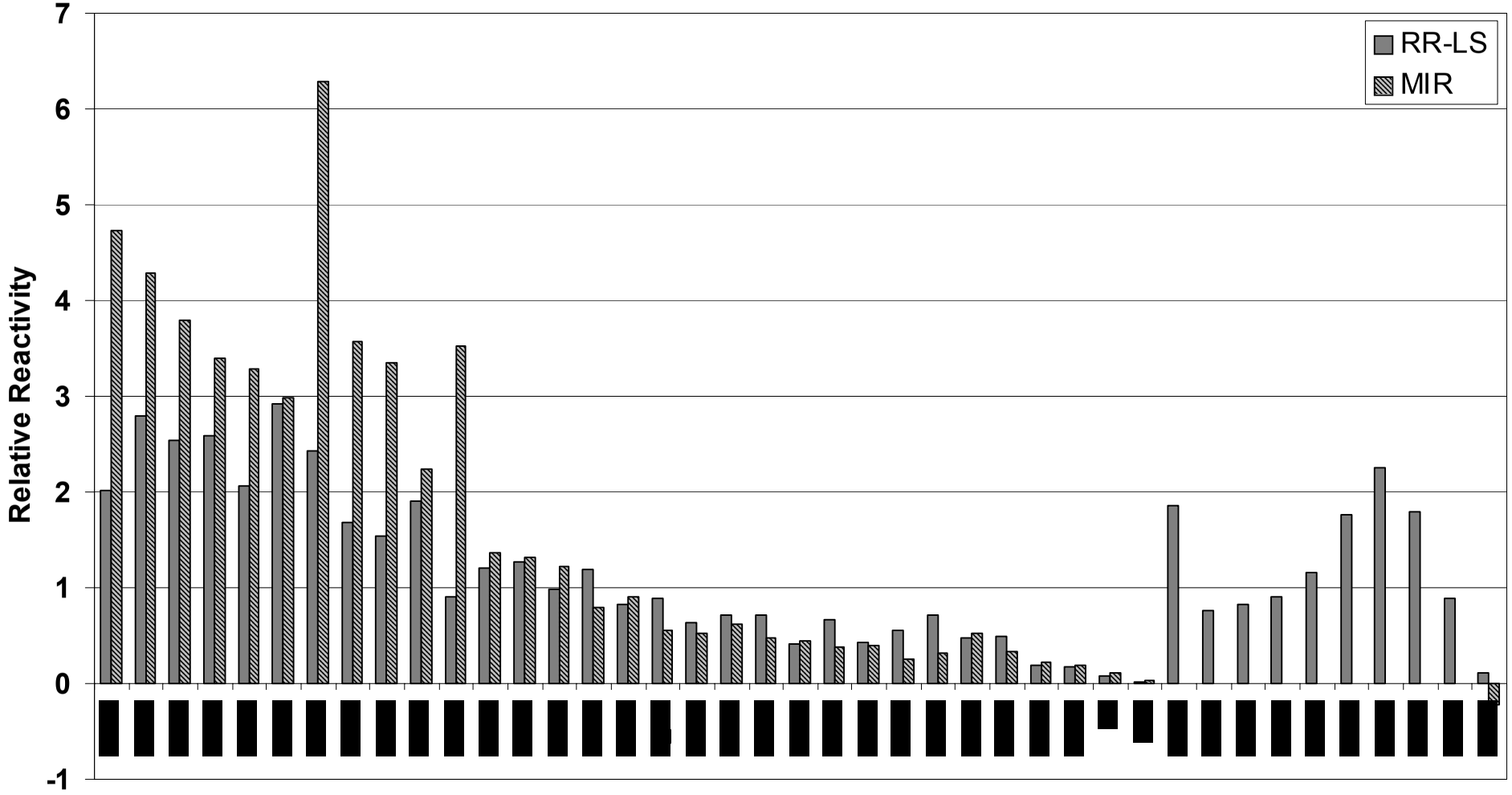


Figure 6 Samples of time series of relative reactivities in 5 urban areas. Relative reactivities are calculated for the cells with base mixture reactivity greater than 0.3 ppb.

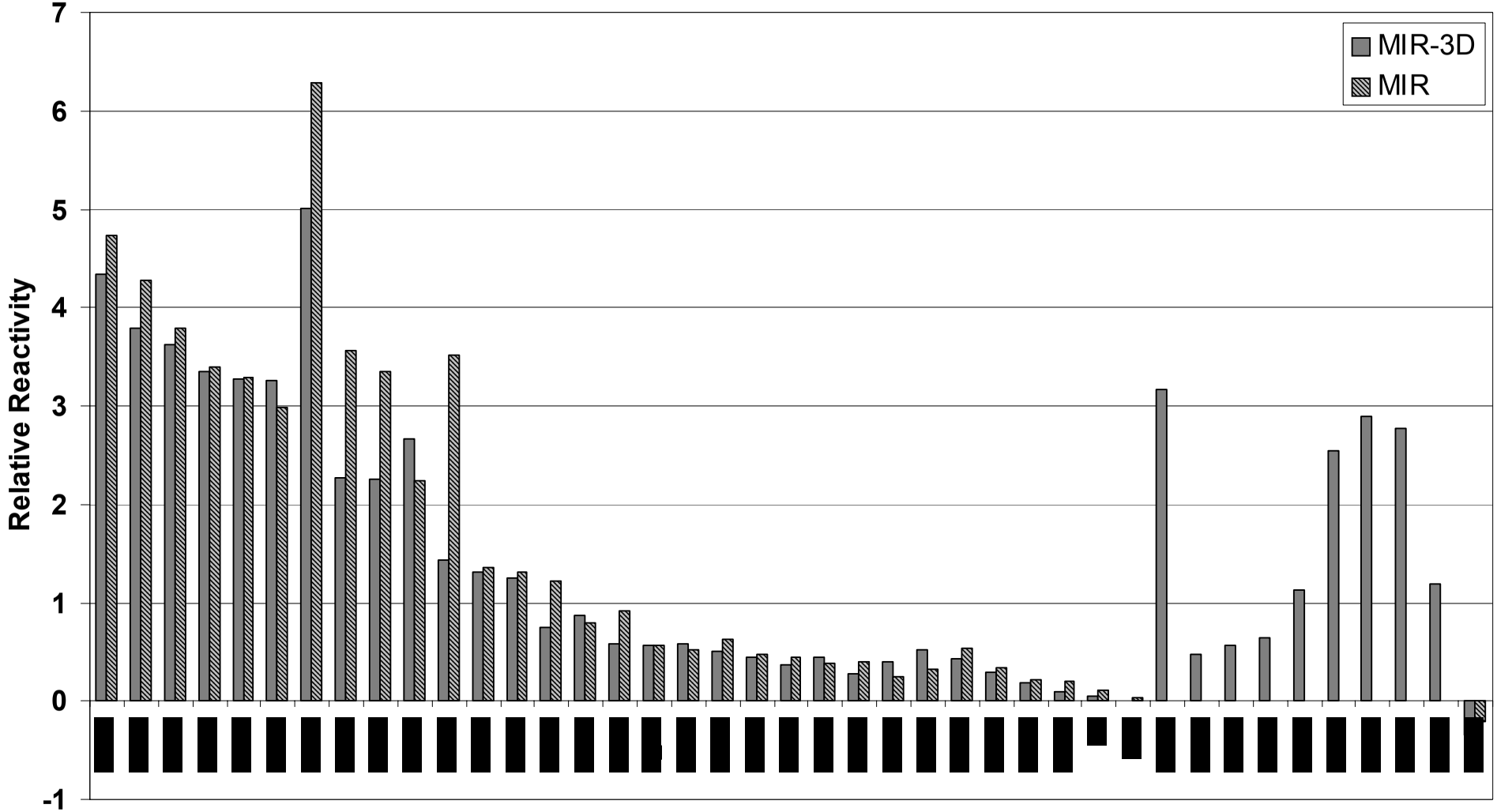
a



b



C



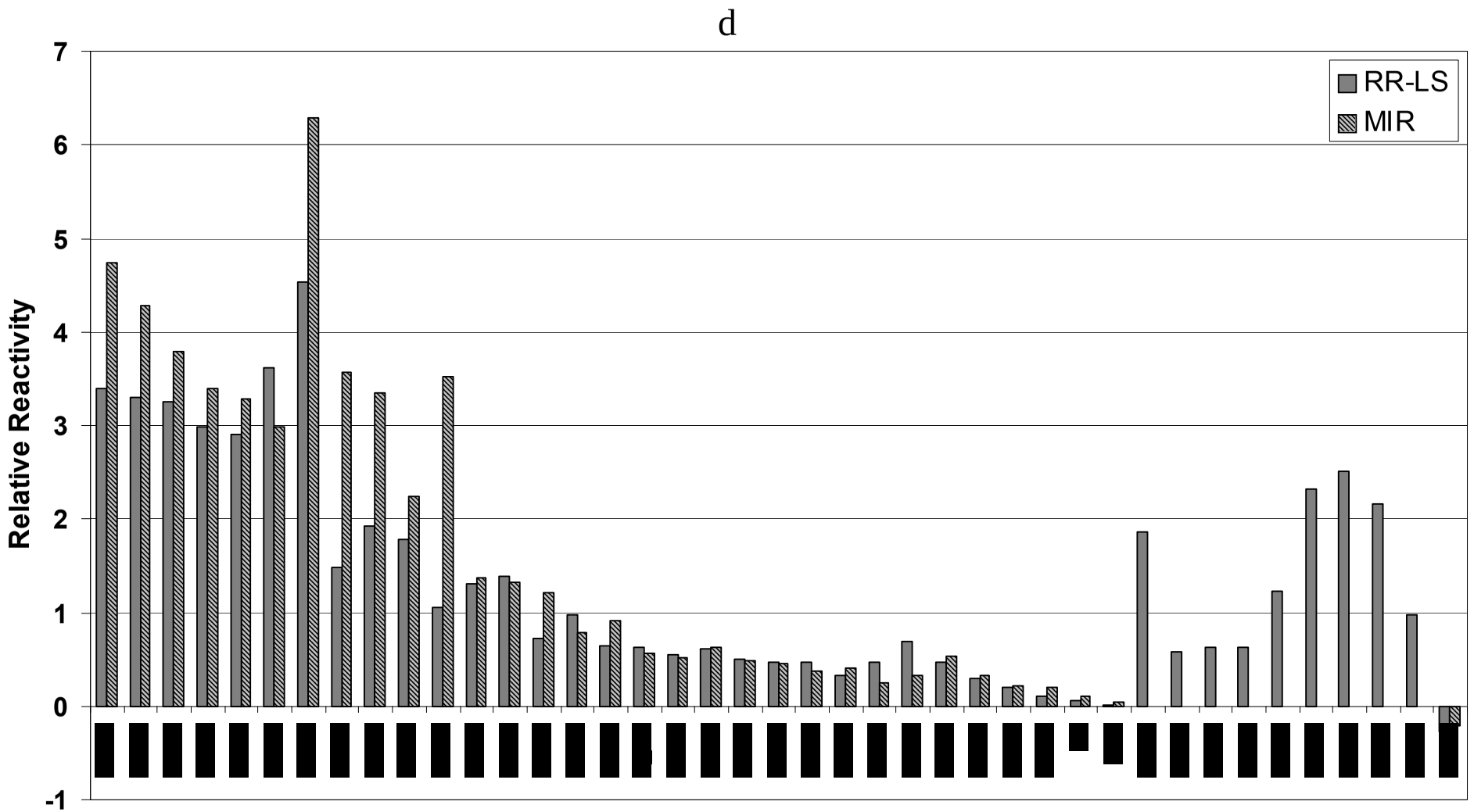
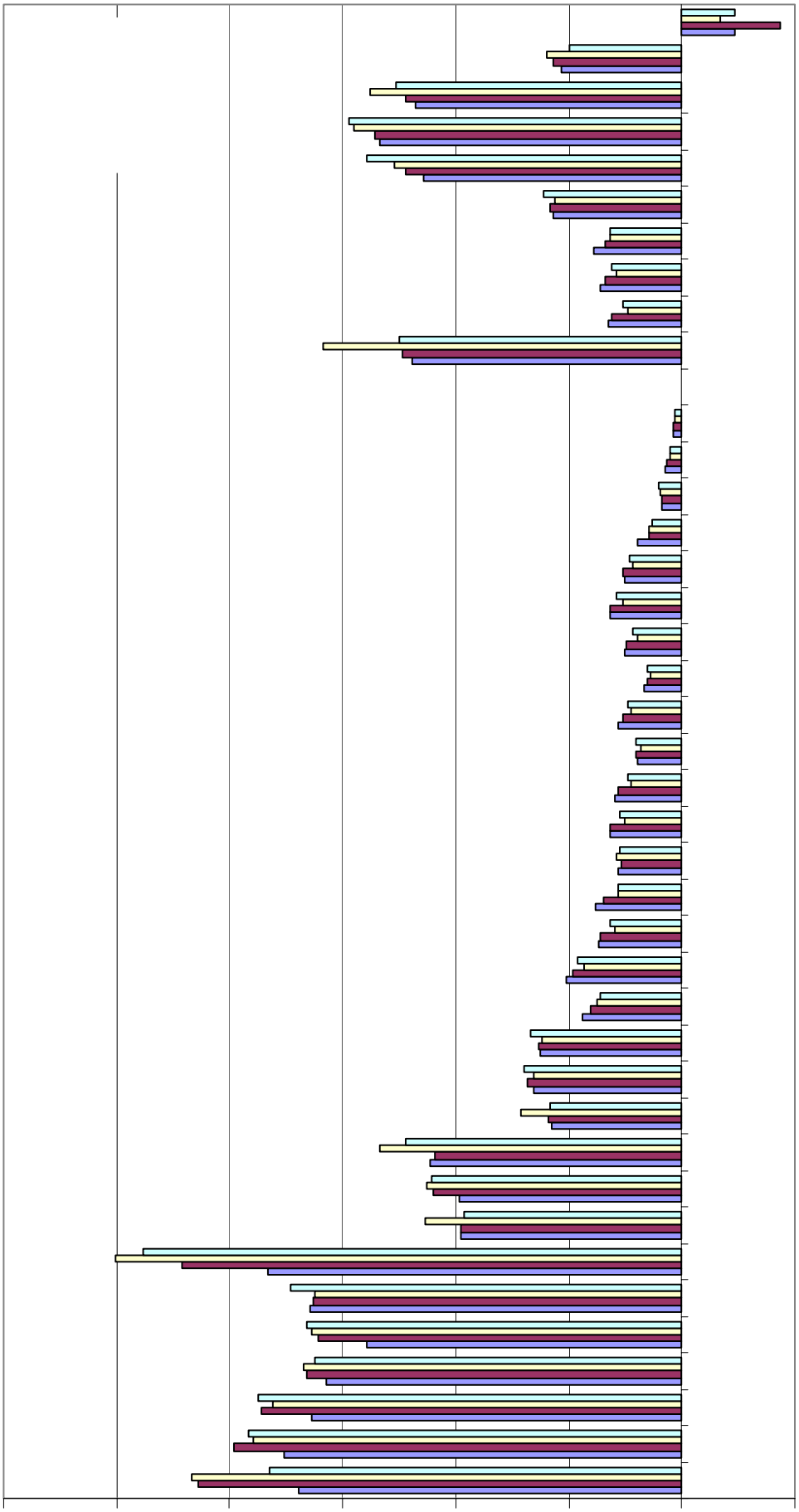
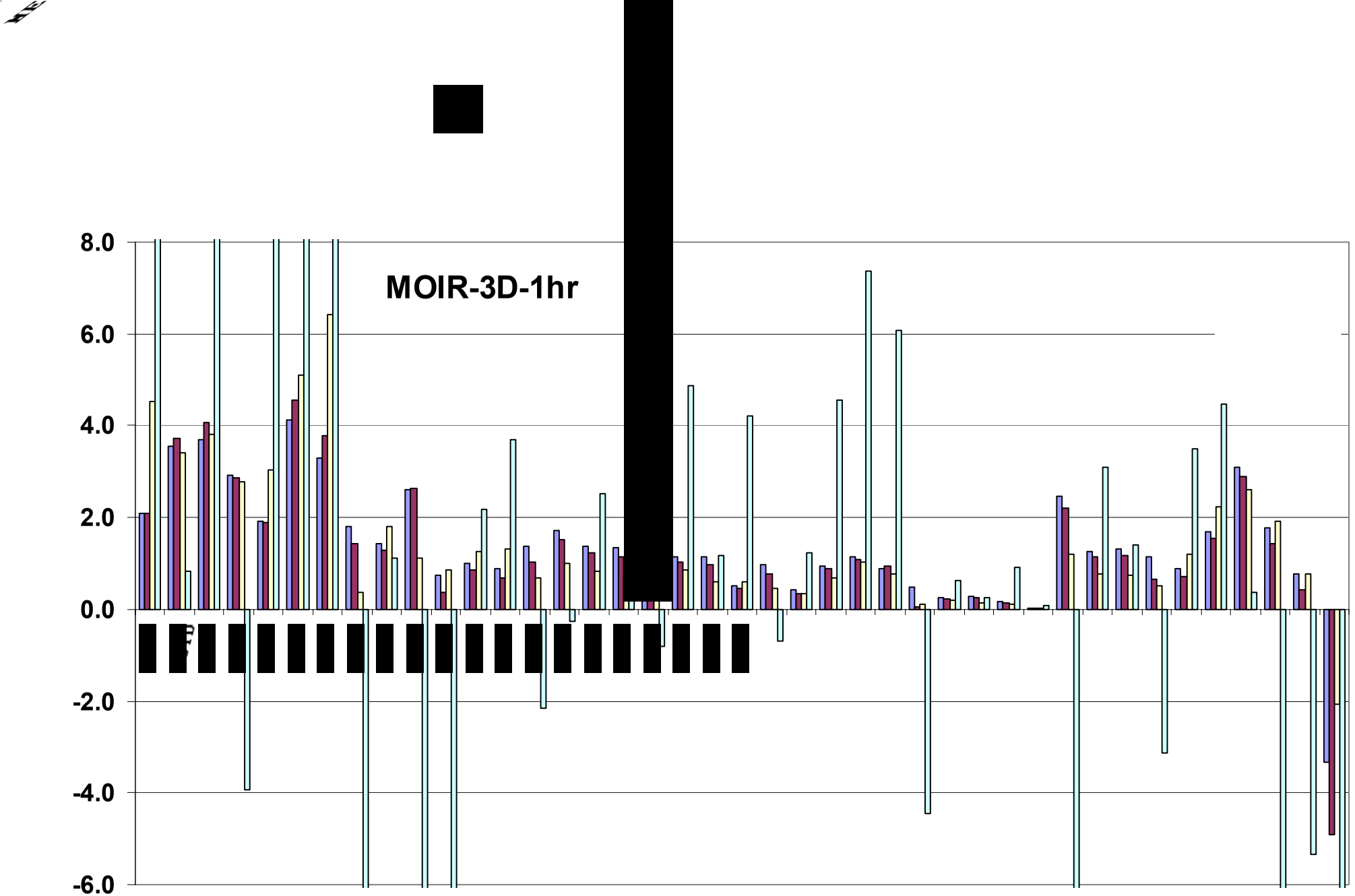
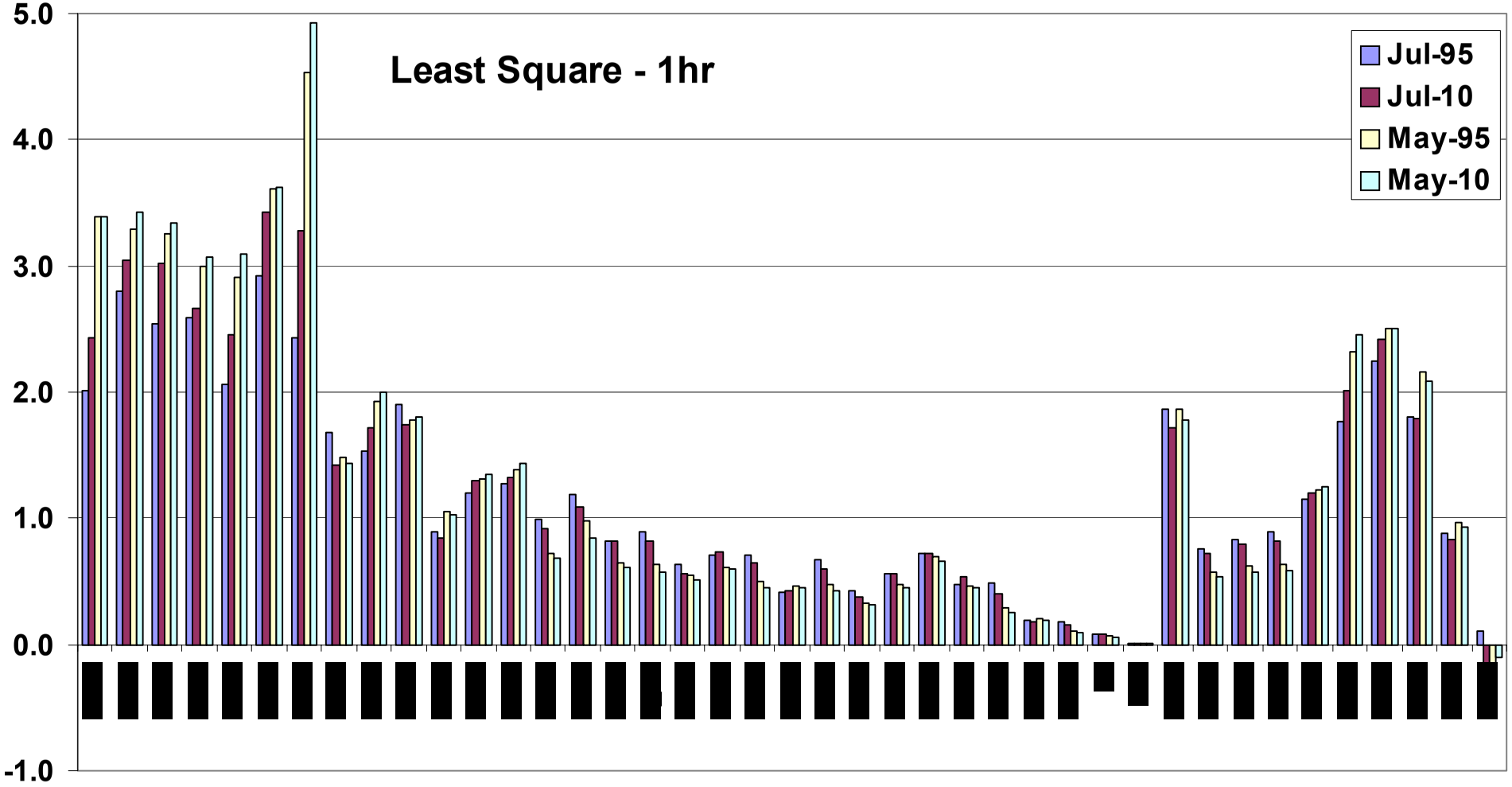


Figure 7 Box Model MIR vs a) MIR-3D, b) LS-RR for July 1995; c) MIR-3D, and d) LS-RR for May 1995 episode.

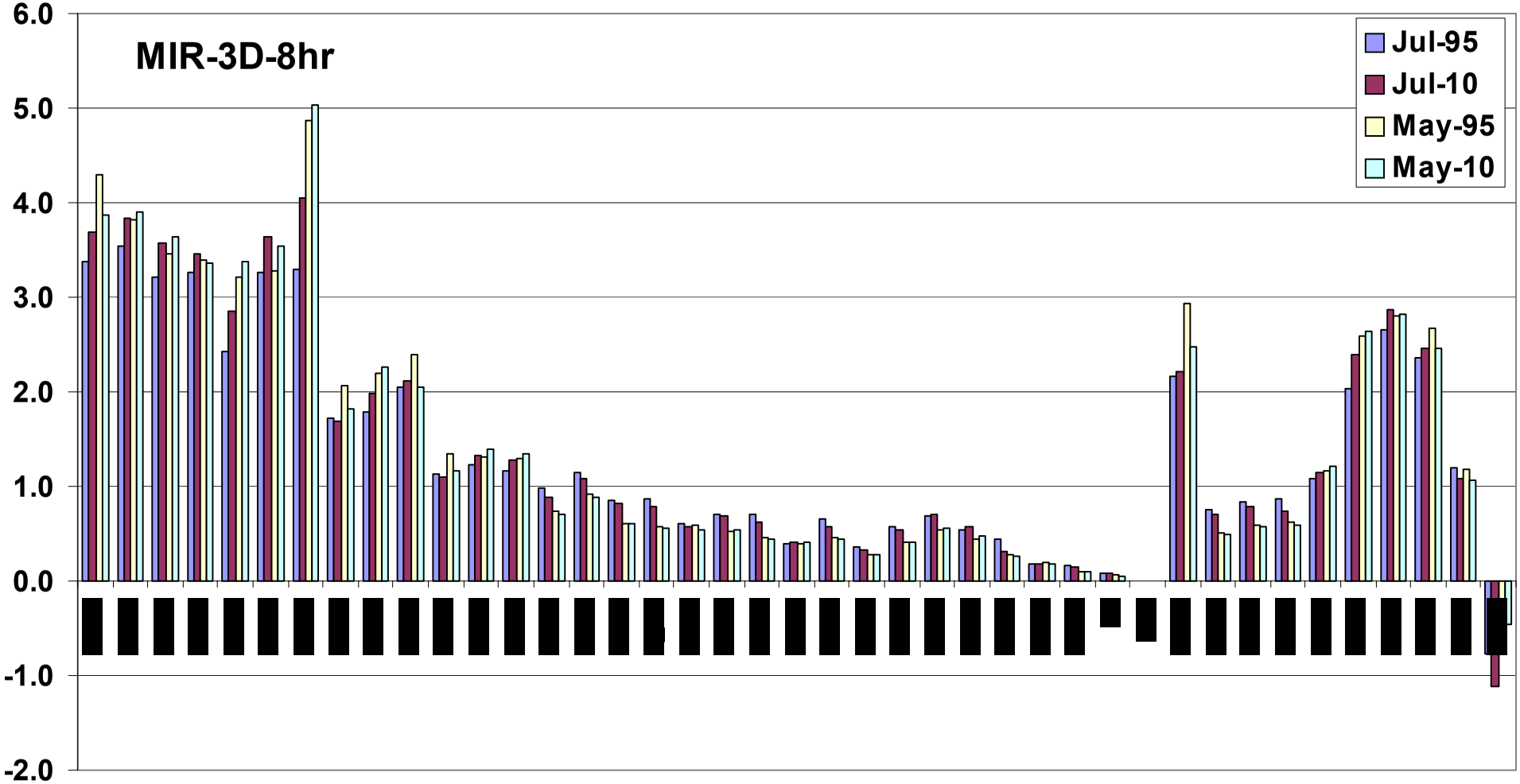


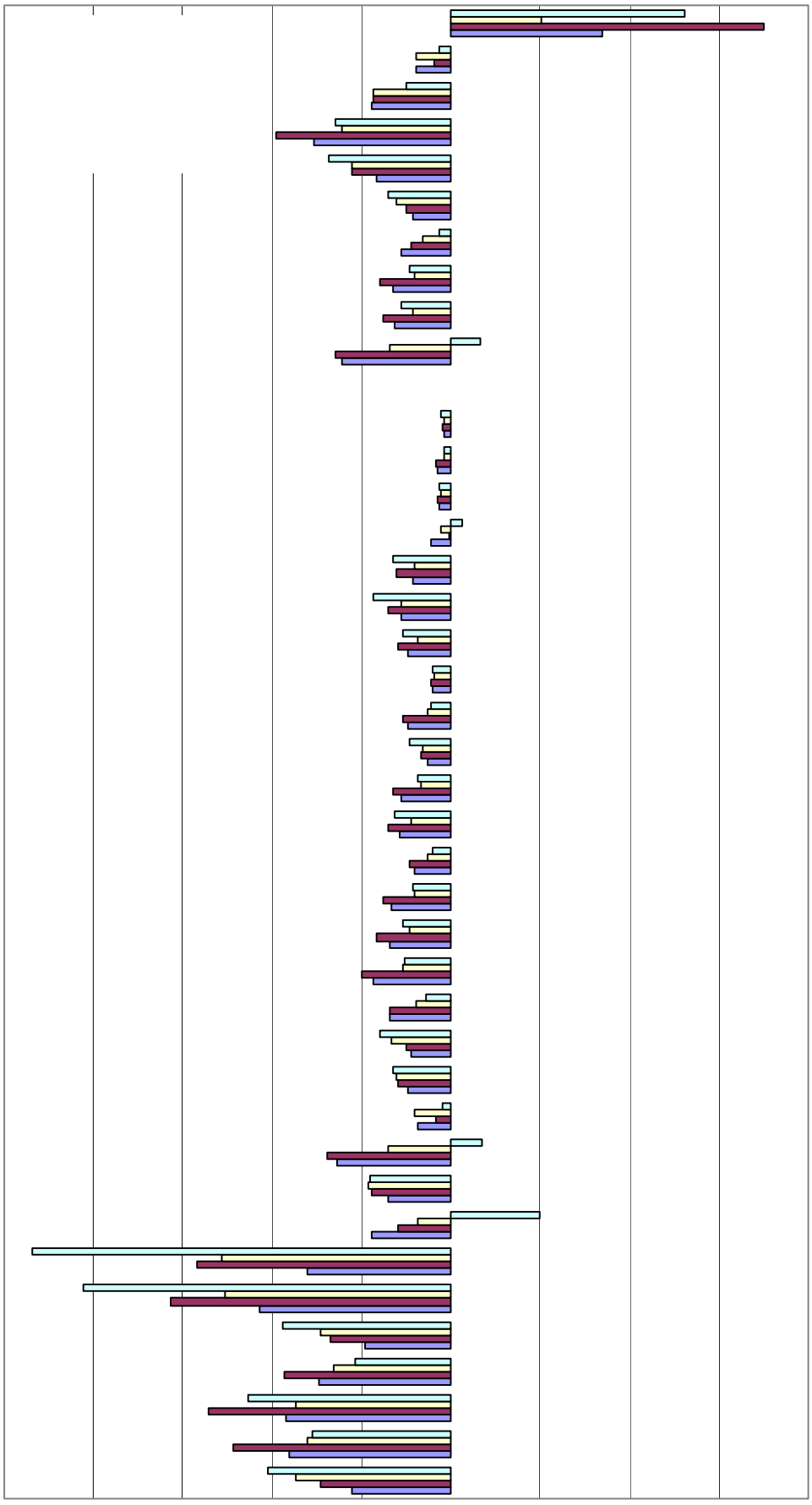

MOIR-3D-1hr
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0

C



d





f

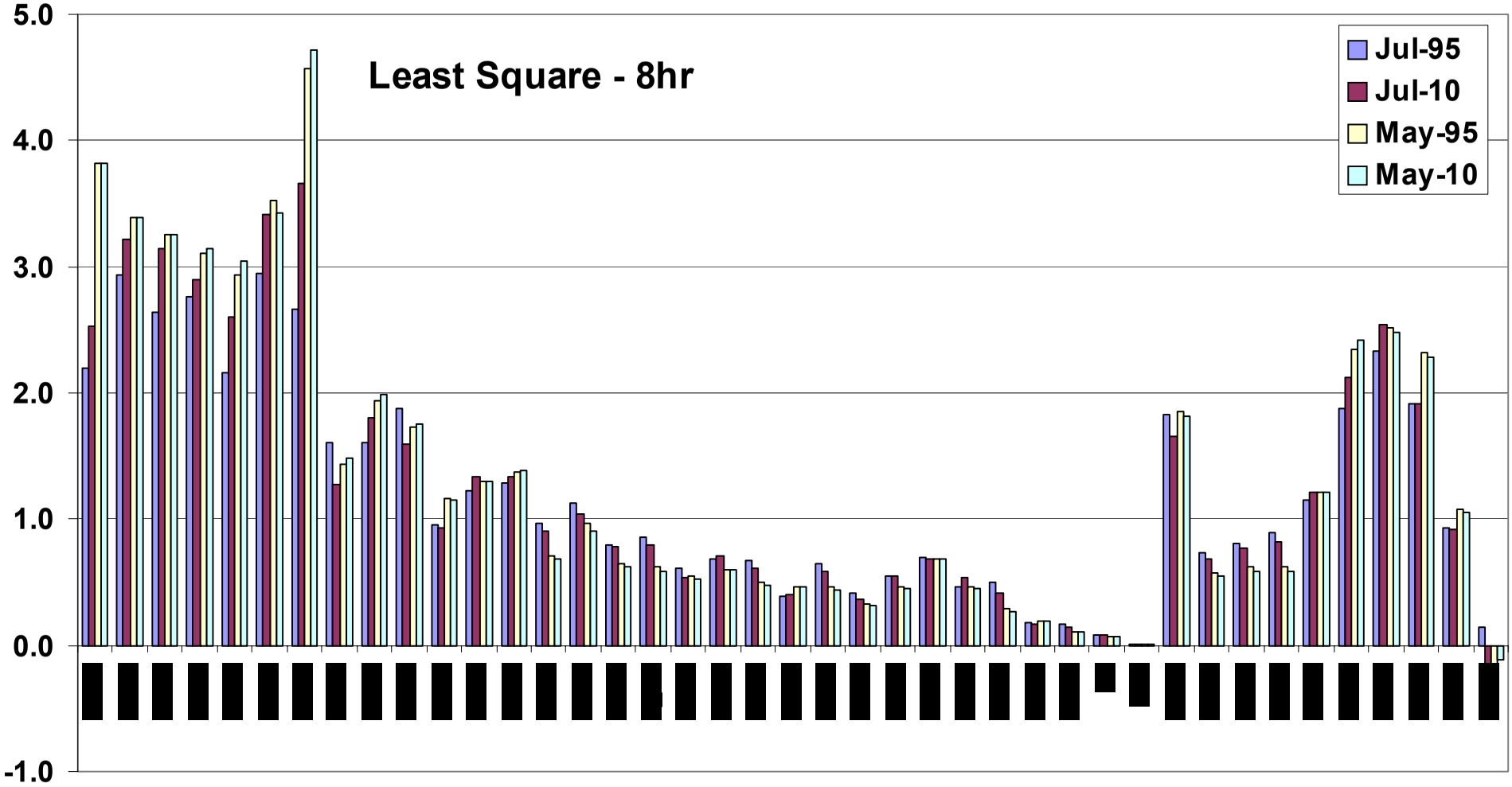


Figure 8 Comparison of different 3-D reactivity metrics for all episodes, a) MIR-$3D_{1hr}$, b) MOIR-$3D_{1hr}$, c) LS-RR_{1hr} , d) MIR-$3D_{8hr}$, e) MOIR-$3D_{8hr}$, and f) LS-RR_{8hr}.

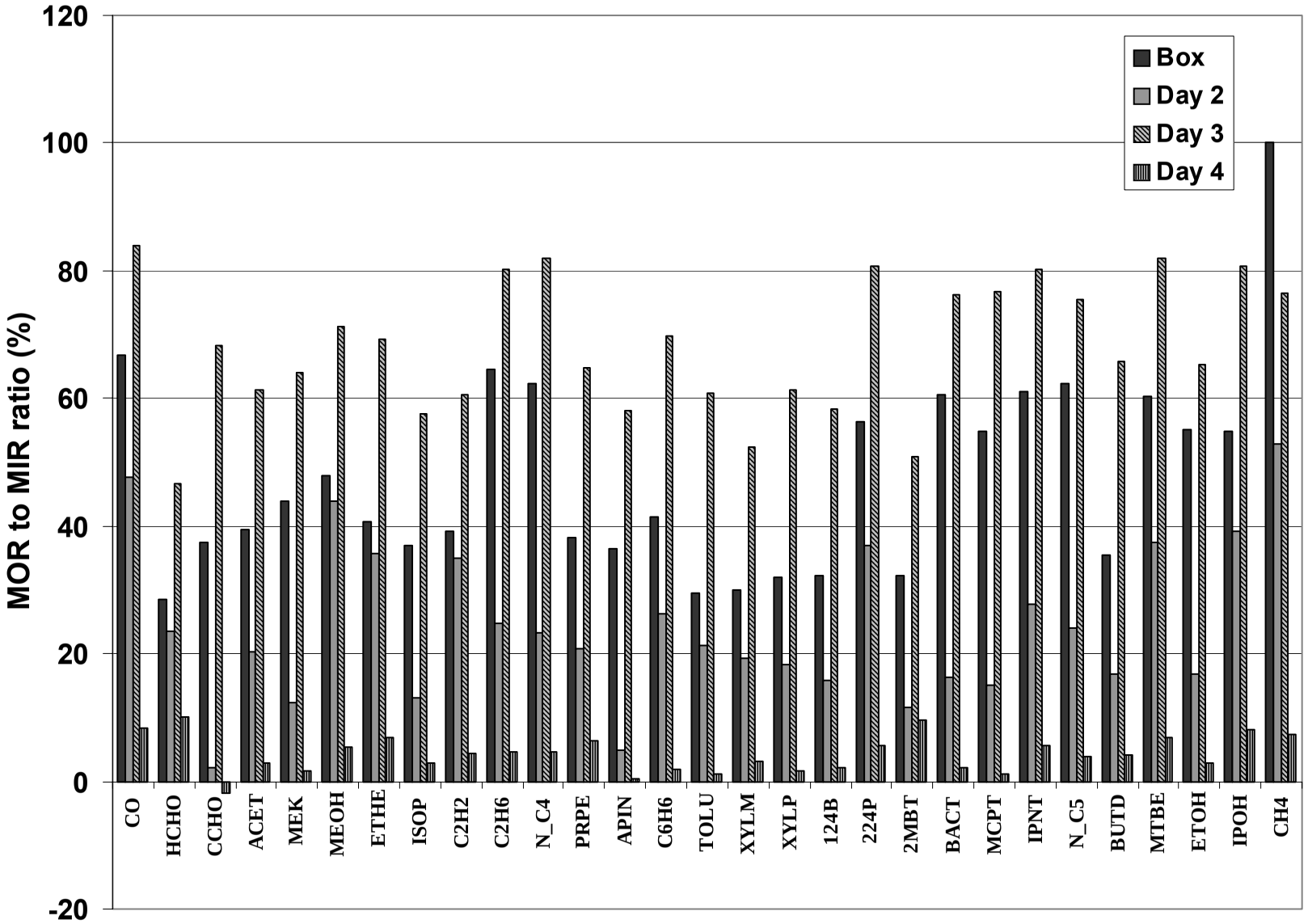
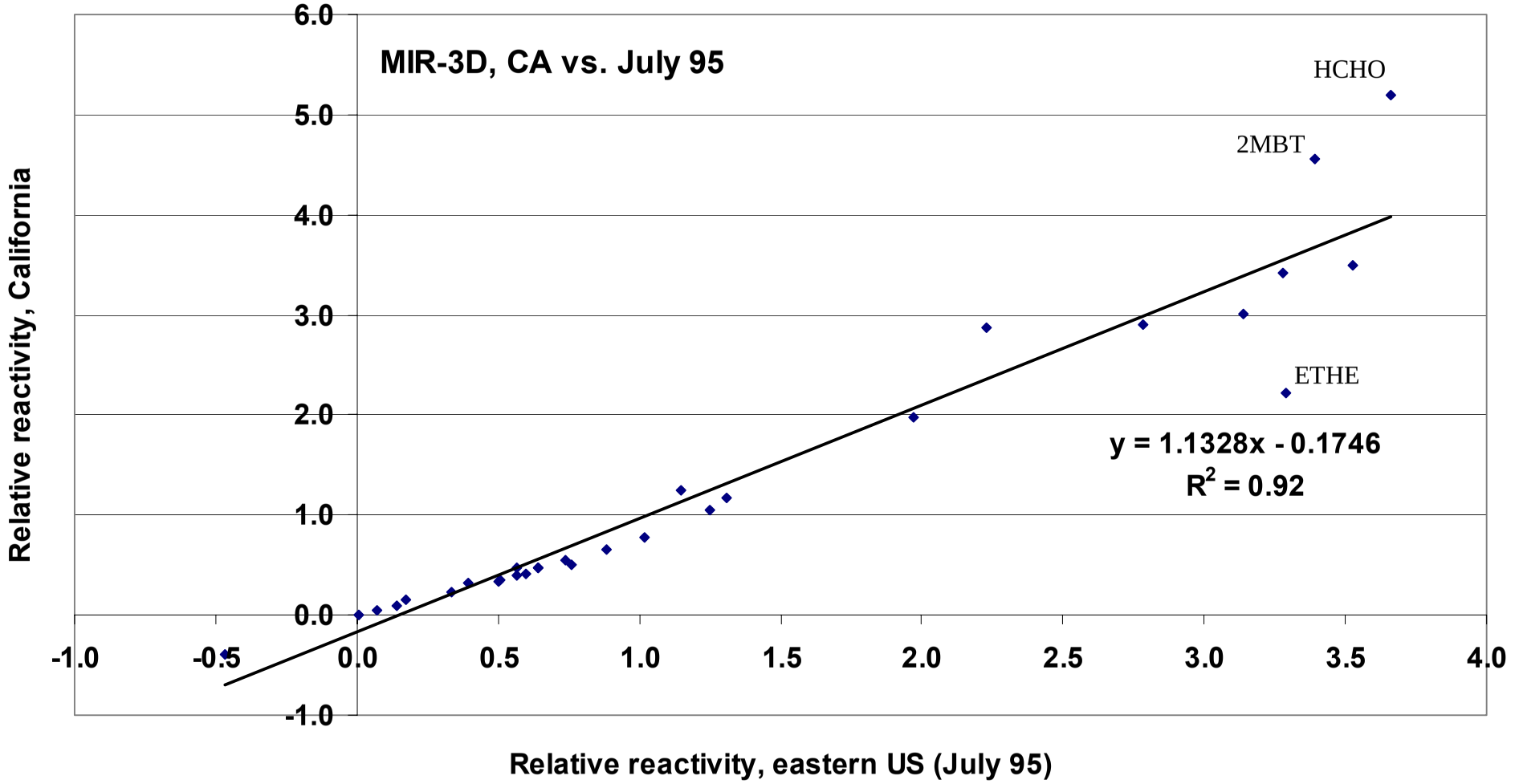


Figure 9 Comparison between ratio of maximum ozone reactivity and maximum reactivity for the box model and different days in 3-D modeling.

a


MIR-3D, CA vs. July 95
HCHO
2MBT
ETHE
y = 1.1328x - 0.1746
R2 = 0.92
Relative reactivity, California
Relative reactivity, eastern US (July 95)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

b

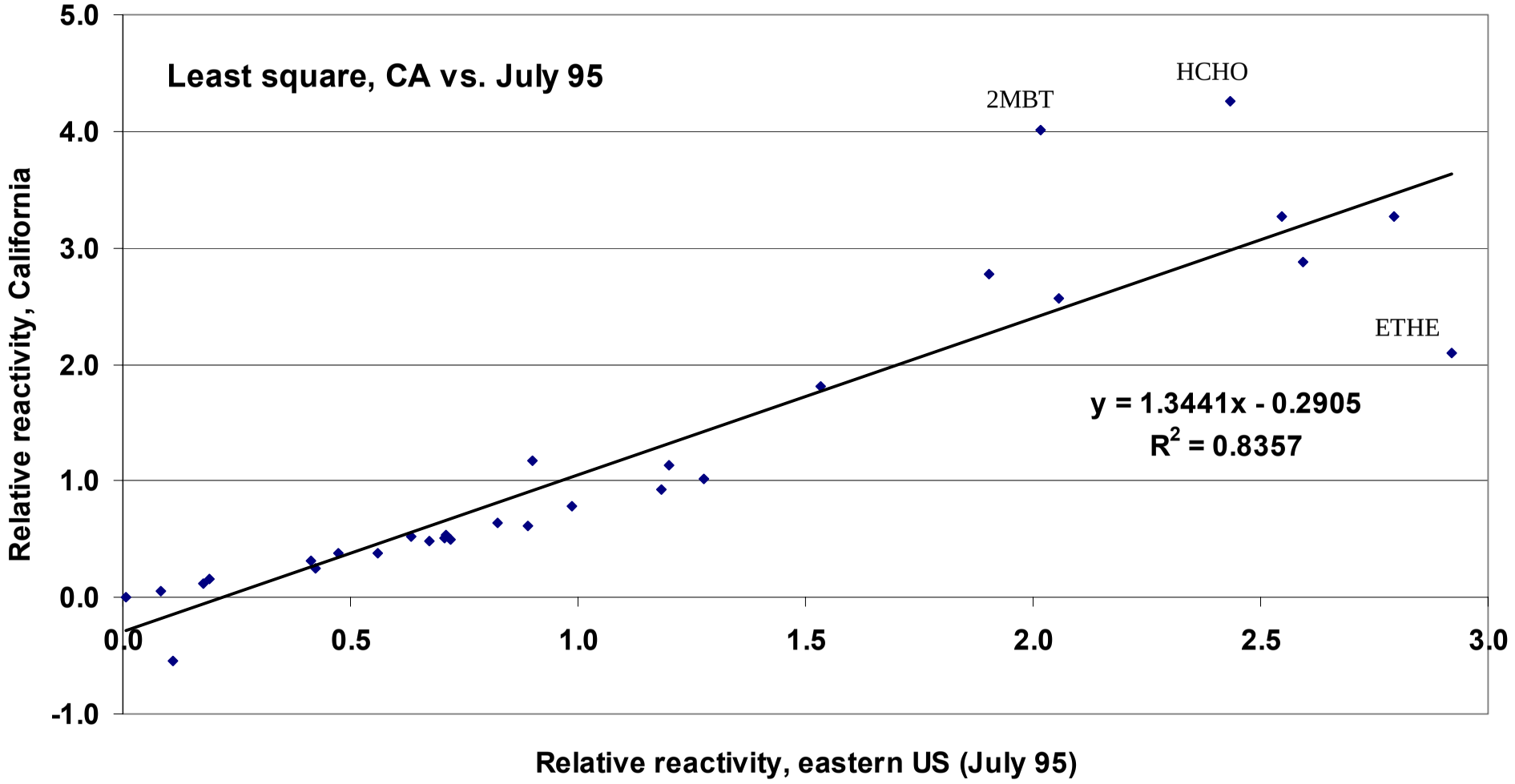
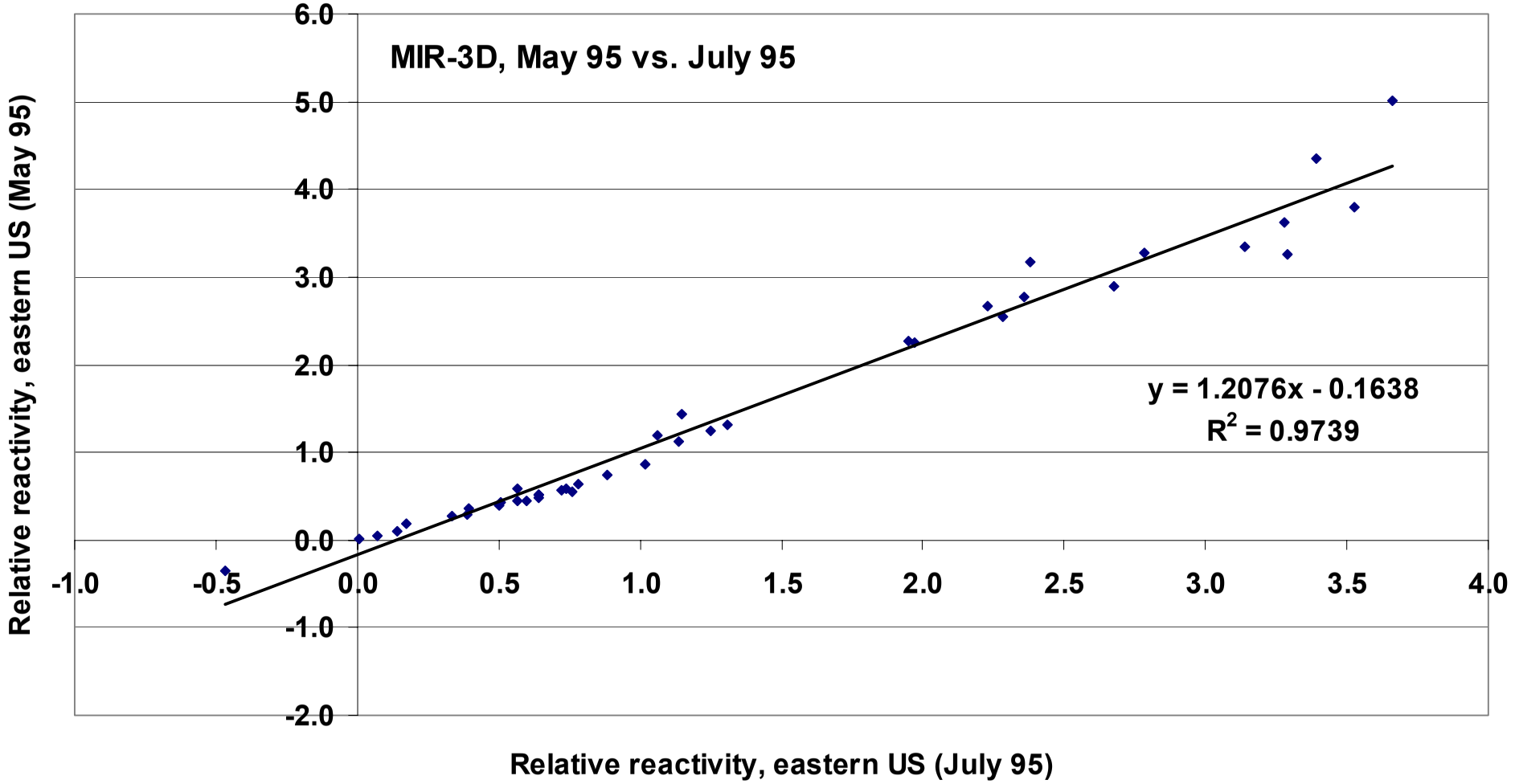


Figure 10 Comparison between Eastern US (July 95) and California for a) MIR-$3D_{1hr}$, and b) LS-RR_{ihr}.

a


MIR-3D, May 95 vs. July 95
y = 1.2076x - 0.1638
R2 = 0.9739
Relative reactivity, eastern US (May 95)
Relative reactivity, eastern US (July 95)
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

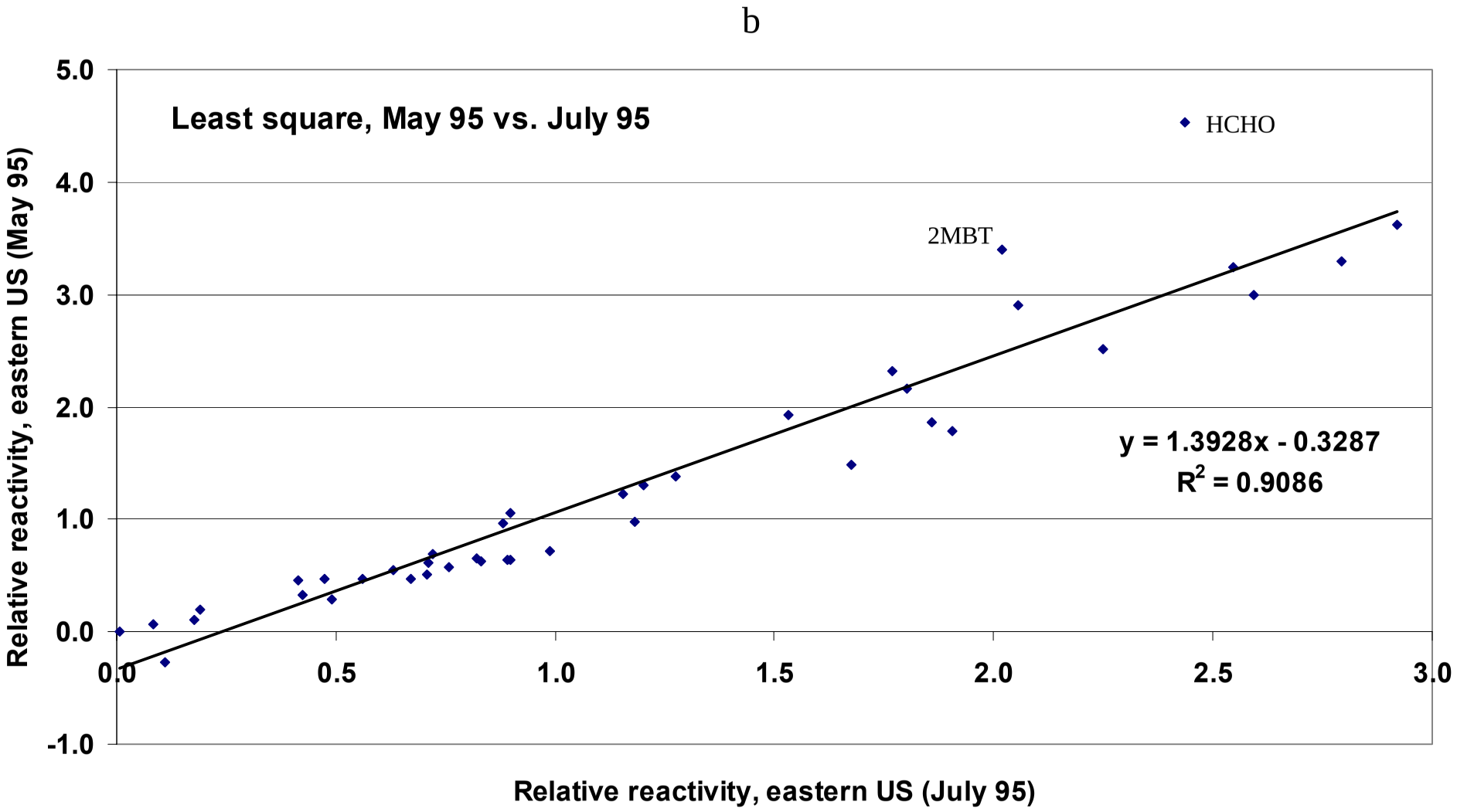
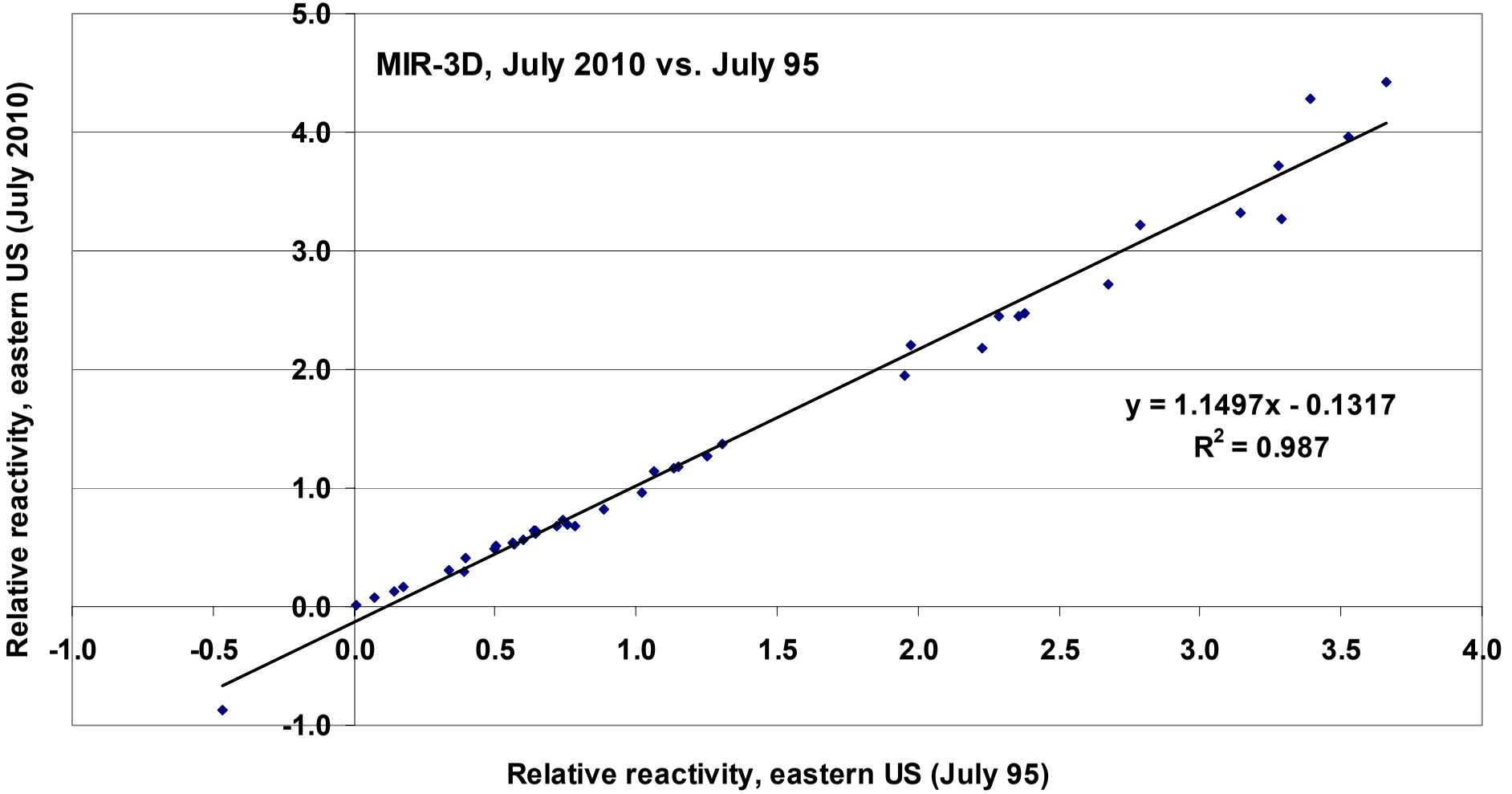


Figure 11 Comparison between different episodes for a) MIR-$3D_{1hr}$, and b) LS-RR_{ihr}.

a


MIR-3D, July 2010 vs. July 95
y = 1.1497x - 0.1317
R2 = 0.987
Relative reactivity, eastern US (July 2010)
Relative reactivity, eastern US (July 95)
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0

b

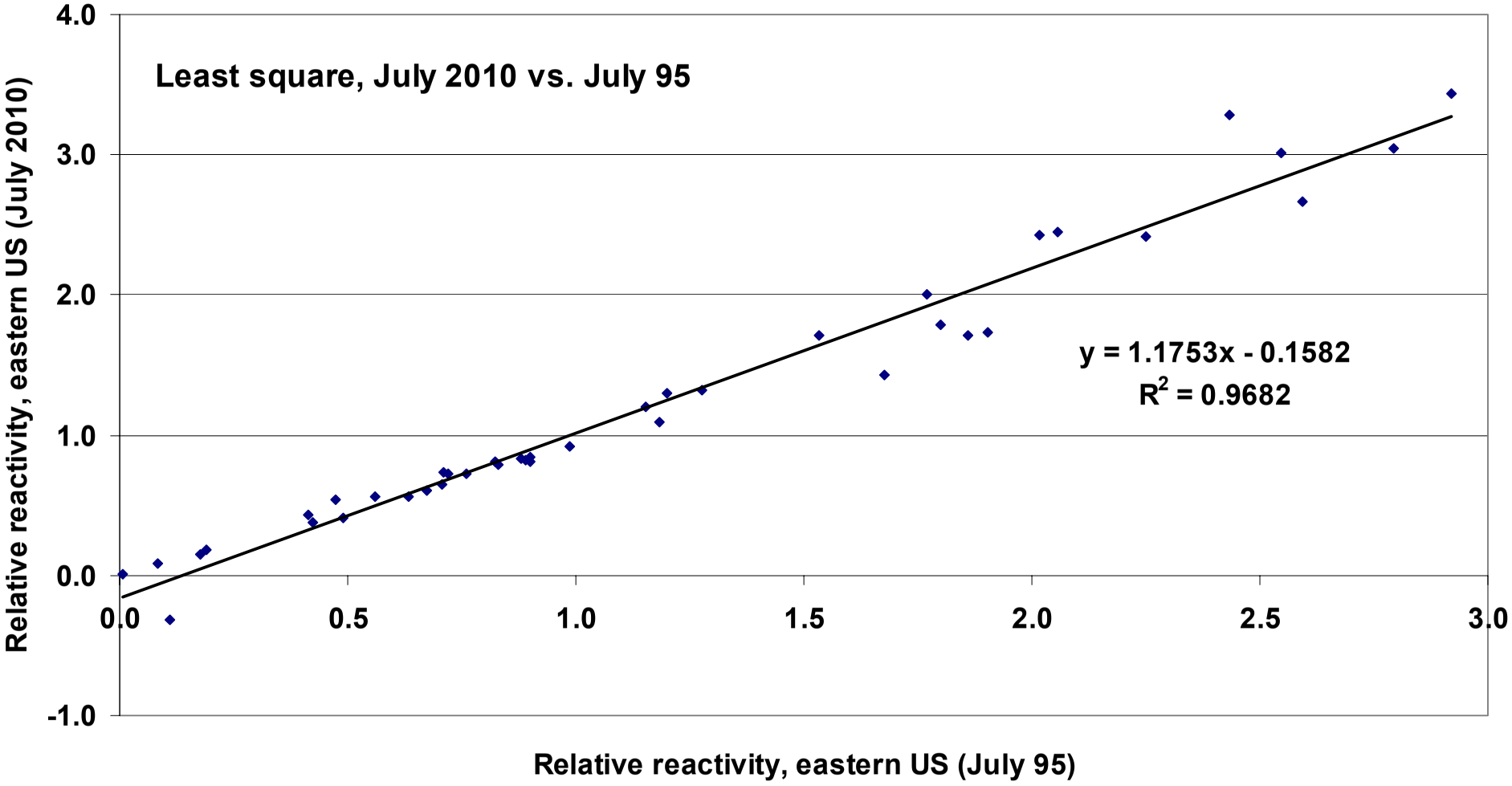
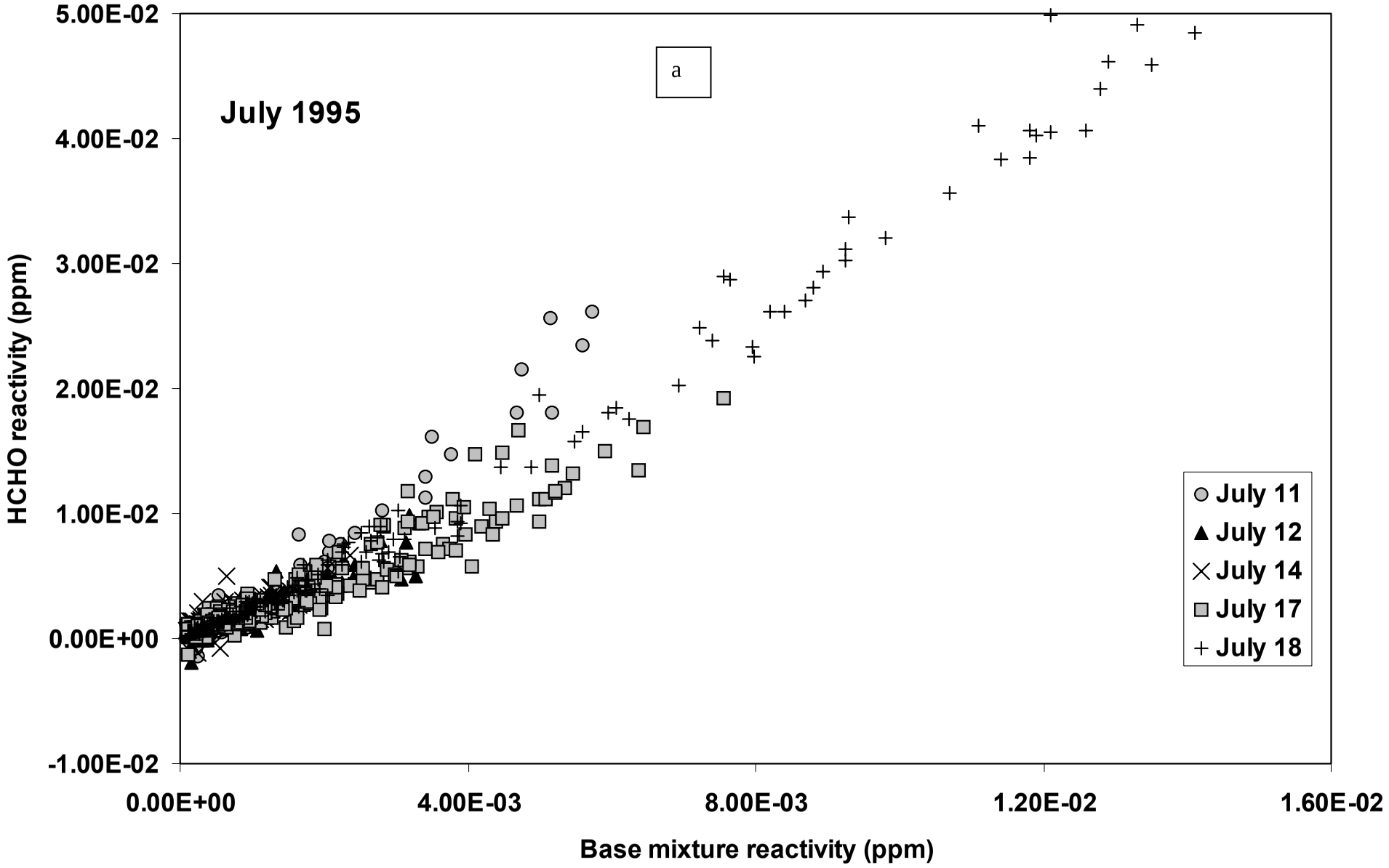
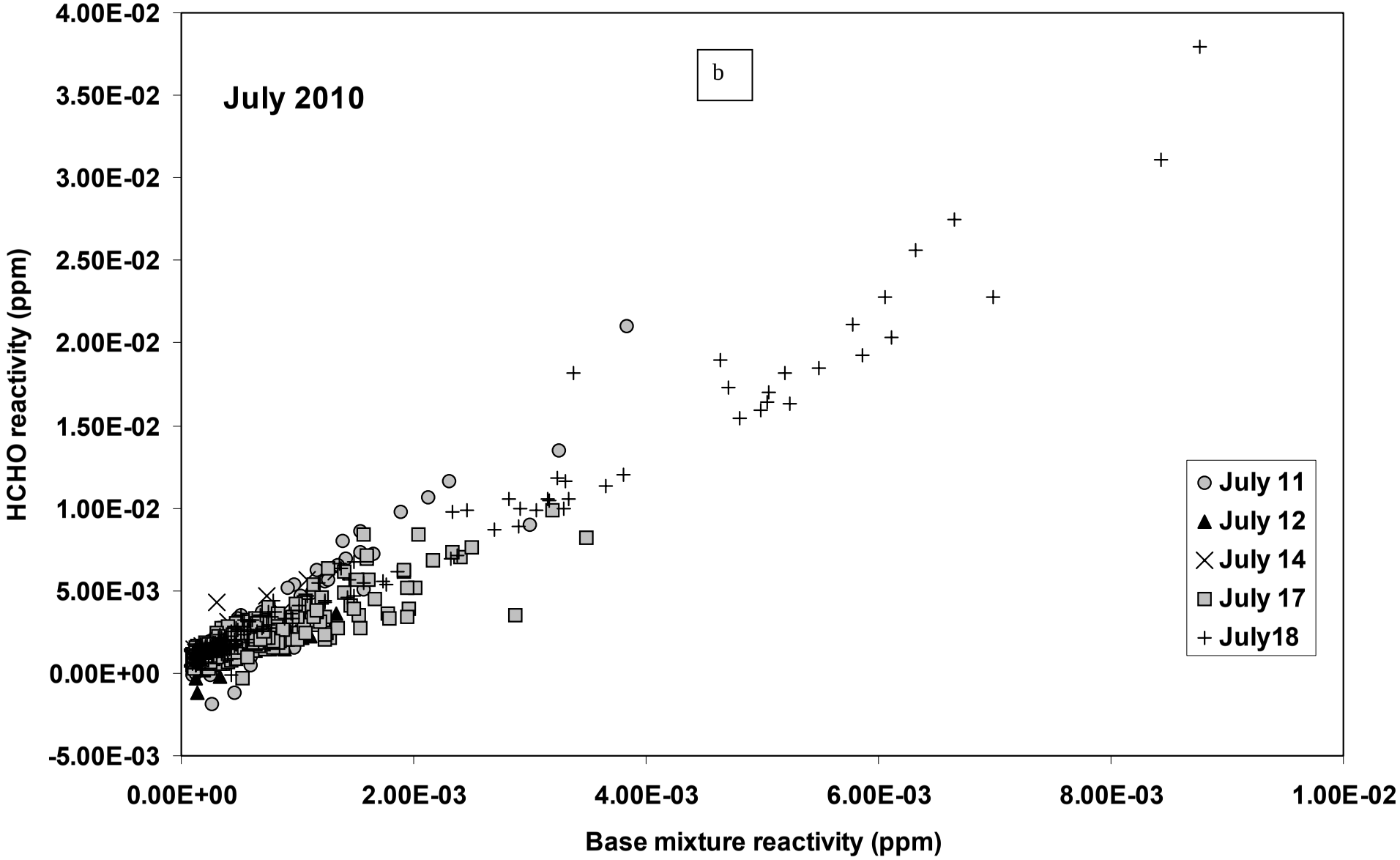
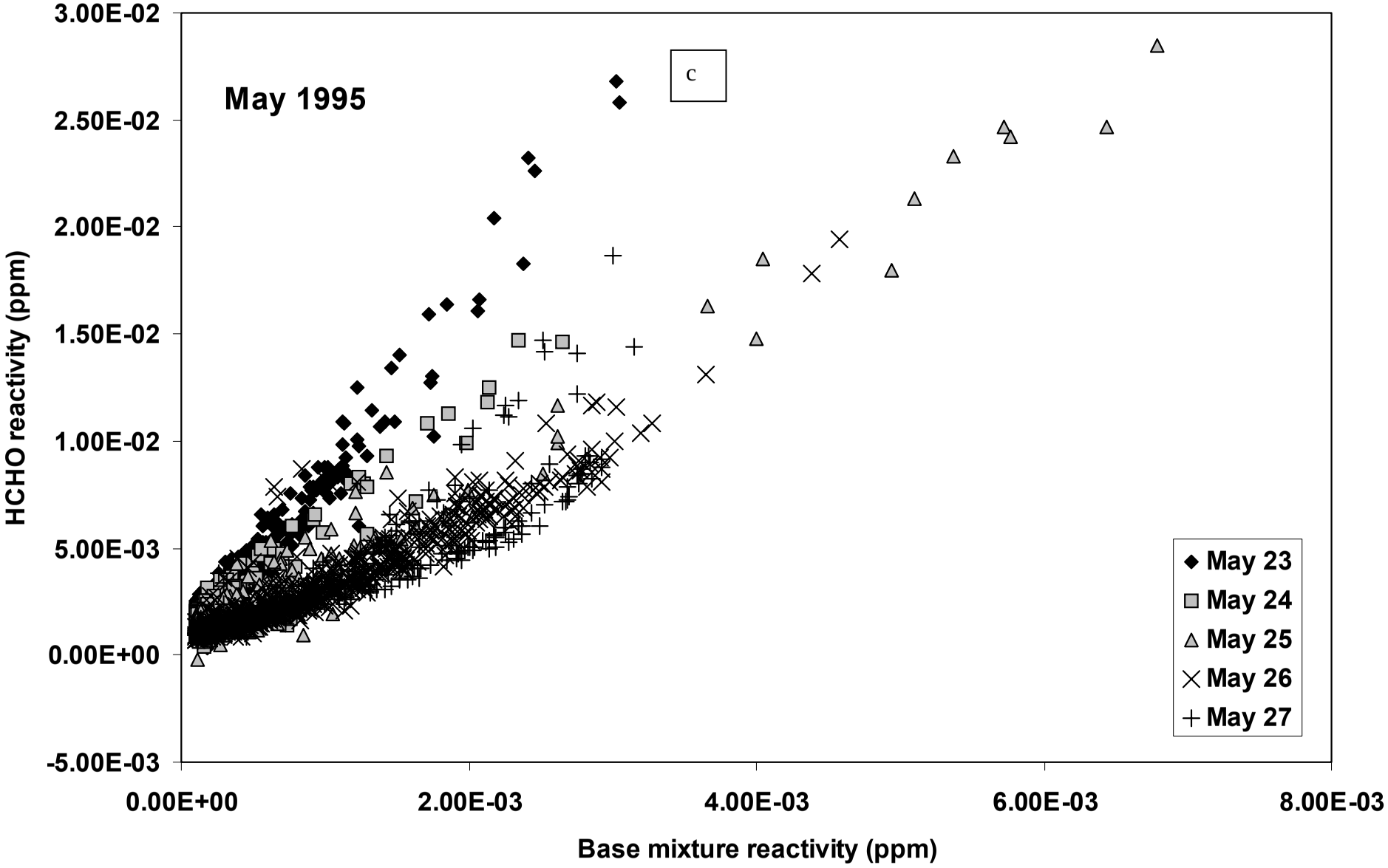


Figure 12 Comparison between different emissions scenarios for a) MIR-$3D_{1hr}$, and b) LS-RR_{1hr}.


a
July 1995
HCHO reactivity (ppm)
5.00E-02
4.00E-02
3.00E-02
2.00E-02
1.00E-02
0.00E+00
-1.00E-02
0.00E+00
4.00E-03
8.00E-03
1.20E-02
1.60E-02
Base mixture reactivity (ppm)
July 11
July 12
July 14
July 17
July 18


b
July 2010
HCHO reactivity (ppm)
Base mixture reactivity (ppm)
4.00E-02
3.50E-02
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
-5.00E-03
0.00E+00
2.00E-03
4.00E-03
6.00E-03
8.00E-03
1.00E-02
July 11
July 12
July 14
July 17
July18


May 1995
c
HCHO reactivity (ppm)
Base mixture reactivity (ppm)
3.00E-02
2.50E-02
2.00E-02
1.50E-02
1.00E-02
5.00E-03
0.00E+00
-5.00E-03
0.00E+00
2.00E-03
4.00E-03
6.00E-03
8.00E-03
May 23
May 24
May 25
May 26
May 27

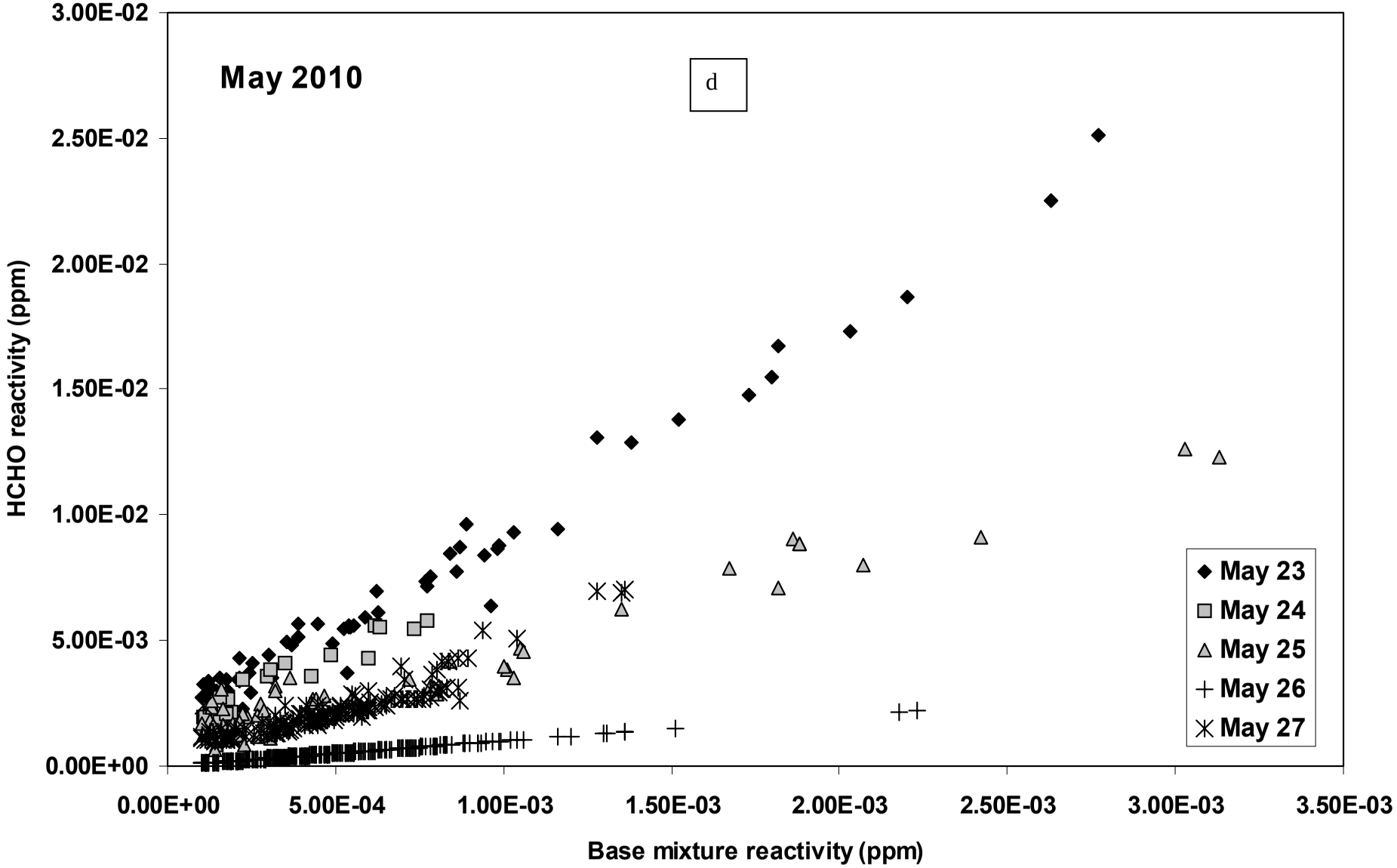


Figure 13 The grid cells and hours used in the calculation of 1-hr least square metrics for a) July 1995, b) July 2010, c) May 1995, and d) May 2010.

Appendix A: Reactivity metrics

Table A1: 1-hr and 8-hr relative MIR-3D and MOIR-3D reactivity metrics for July 1995.

		MIR-3D		MOIR-3D		MIR-3D-8hr		MOIR-3D-8hr	
Species	**MIR**	**mean**	**stdev**	**mean**	**stdev**	**mean**	**stdev**	**mean**	**stdev**
2MBT	14.450	3.390	0.778	2.082	1.255	3.370	1.320	2.235	1.258
BUTD	13.580	3.524	0.287	3.556	0.598	3.546	0.520	3.625	0.730
PRPE	11.580	3.280	0.347	3.684	1.021	3.217	0.354	3.710	1.031
ISOP	10.690	3.141	0.301	2.916	0.366	3.262	0.632	2.948	0.491
XYLM	10.610	2.786	0.509	1.913	0.673	2.429	0.374	1.915	0.597
ETHE	9.080	3.288	0.294	4.140	1.203	3.256	0.185	4.293	0.962
HCHO	8.970	3.663	0.807	3.284	1.366	3.302	0.846	3.227	1.215
ACRO	7.610	1.951	0.547	1.798	1.183	1.729	0.570	1.762	1.114
124B	7.180	1.973	0.276	1.426	0.471	1.783	0.227	1.417	0.404
CCHO	6.840	2.230	0.391	2.606	0.804	2.049	0.557	2.550	0.898
APIN	4.290	1.148	0.134	0.747	0.471	1.136	0.239	0.737	0.412
XYLP	4.250	1.308	0.080	0.999	0.439	1.233	0.102	0.981	0.335
TOLU	3.970	1.250	0.083	0.898	0.551	1.171	0.153	0.892	0.375
MCPT	2.420	0.884	0.108	1.369	0.396	0.988	0.145	1.352	0.287
ETOH	1.690	1.018	0.112	1.731	0.572	1.154	0.156	1.725	0.396
IPNT	1.670	0.740	0.099	1.382	0.574	0.854	0.164	1.369	0.427
N_C5	1.540	0.758	0.111	1.357	0.534	0.875	0.186	1.349	0.414
MEK	1.480	0.564	0.067	0.799	0.246	0.610	0.069	0.822	0.187
224P	1.440	0.640	0.067	1.151	0.510	0.711	0.117	1.146	0.402
N_C4	1.330	0.599	0.094	1.144	0.490	0.700	0.153	1.128	0.349
C2H2	1.250	0.394	0.046	0.516	0.128	0.395	0.044	0.533	0.108
BACT	0.890	0.566	0.062	0.980	0.344	0.662	0.125	0.971	0.263
C6H6	0.820	0.335	0.048	0.414	0.066	0.361	0.054	0.423	0.054
MTBE	0.780	0.499	0.067	0.948	0.479	0.572	0.123	0.946	0.372
MEOH	0.710	0.642	0.069	1.131	0.536	0.687	0.094	1.124	0.393
IPOH	0.710	0.504	0.059	0.886	0.492	0.541	0.092	0.870	0.371
DODC	0.660	0.390	0.073	0.481	0.125	0.447	0.063	0.445	0.125
ACET	0.430	0.176	0.023	0.245	0.057	0.183	0.014	0.250	0.041
C2H6	0.310	0.140	0.028	0.293	0.140	0.170	0.046	0.293	0.099
CO	0.060	0.072	0.011	0.162	0.112	0.084	0.021	0.158	0.079
CH4	0.010	0.007	0.001	0.015	0.009	0.008	0.002	0.015	0.006
RCHO	N/A	2.380	0.544	2.462	0.951	2.158	0.534	2.456	0.846
AAR1	N/A	0.643	0.090	1.271	0.566	0.747	0.154	1.267	0.418
AAR2	N/A	0.721	0.091	1.327	0.528	0.830	0.150	1.307	0.382
ALK3	N/A	0.784	0.097	1.146	0.364	0.875	0.132	1.109	0.272
ARO1	N/A	1.135	0.053	0.873	0.418	1.087	0.112	0.870	0.286
AAR3	N/A	2.286	0.392	1.683	0.507	2.029	0.331	1.672	0.475
OLE1	N/A	2.676	0.235	3.091	0.545	2.657	0.266	3.083	0.495
OLE2	N/A	2.356	0.293	1.773	0.768	2.361	0.564	1.777	0.726
TRP1	N/A	1.063	0.107	0.776	0.369	1.196	0.444	0.761	0.339
BALD	-0.610	-0.467	0.373	-3.329	2.840	-0.770	0.700	-3.386	2.146

Table A2: 1-hr and 8-hr relative MIR-3D and MOIR-3D reactivity metrics for May 1995.

Species	MIR	MIR-3D		MOIR-3D		MIR-3D-8hr		MOIR-3D-8hr	
		mean	stdev	mean	stdev	mean	stdev	mean	stdev
2MBT	14.450	4.343	0.712	4.539	2.705	4.290	1.227	3.483	1.307
BUTD	13.580	3.794	0.584	3.406	0.676	3.815	0.646	3.223	0.416
PRPE	11.580	3.617	0.082	3.809	0.798	3.458	0.403	3.456	0.626
ISOP	10.690	3.347	0.573	2.766	0.623	3.387	0.602	2.630	0.407
XYLM	10.610	3.268	0.531	3.026	0.918	3.215	0.510	2.900	1.091
ETHE	9.080	3.251	0.276	5.103	1.730	3.273	0.234	5.062	0.961
HCHO	8.970	5.011	0.615	6.423	3.682	4.870	1.108	5.123	2.588
ACRO	7.610	2.276	0.199	0.370	1.499	2.058	0.259	0.750	0.903
124B	7.180	2.257	0.323	1.813	0.338	2.197	0.331	1.837	0.398
CCHO	6.840	2.666	0.197	1.125	1.128	2.393	0.318	1.415	0.889
APIN	4.290	1.428	0.240	0.844	0.369	1.348	0.304	0.799	0.193
XYLP	4.250	1.316	0.123	1.264	0.172	1.314	0.092	1.238	0.193
TOLU	3.970	1.244	0.071	1.306	0.280	1.295	0.113	1.328	0.173
MCPT	2.420	0.746	0.067	0.687	0.352	0.741	0.074	0.767	0.321
ETOH	1.690	0.868	0.119	0.997	0.394	0.919	0.219	1.063	0.403
IPNT	1.670	0.588	0.073	0.833	0.189	0.601	0.094	0.913	0.303
N_C5	1.540	0.559	0.082	0.748	0.242	0.579	0.114	0.805	0.281
MEK	1.480	0.578	0.011	0.502	0.154	0.586	0.089	0.510	0.116
224P	1.440	0.508	0.067	0.853	0.194	0.522	0.084	0.895	0.179
N_C4	1.330	0.450	0.072	0.611	0.206	0.464	0.099	0.666	0.260
C2H2	1.250	0.362	0.035	0.589	0.237	0.389	0.081	0.619	0.119
BACT	0.890	0.445	0.054	0.467	0.244	0.456	0.080	0.531	0.240
C6H6	0.820	0.272	0.041	0.349	0.086	0.284	0.063	0.379	0.068
MTBE	0.780	0.396	0.063	0.694	0.172	0.407	0.074	0.757	0.222
MEOH	0.710	0.520	0.118	1.026	0.312	0.547	0.144	1.121	0.323
IPOH	0.710	0.429	0.023	0.758	0.211	0.438	0.034	0.805	0.209
DODC	0.660	0.293	0.078	0.120	0.318	0.281	0.068	0.214	0.255
ACET	0.430	0.194	0.005	0.211	0.038	0.197	0.031	0.215	0.023
C2H6	0.310	0.098	0.022	0.136	0.056	0.101	0.026	0.154	0.073
CO	0.060	0.055	0.011	0.114	0.041	0.058	0.010	0.134	0.057
CH4	0.010	0.005	0.001	0.010	0.003	0.005	0.001	0.012	0.004
RCHO	N/A	3.170	0.541	1.197	1.195	2.941	0.662	1.373	0.756
AAR1	N/A	0.481	0.077	0.758	0.213	0.508	0.110	0.850	0.308
AAR2	N/A	0.571	0.078	0.740	0.229	0.587	0.103	0.805	0.283
ALK3	N/A	0.639	0.102	0.526	0.377	0.623	0.093	0.635	0.337
ARO1	N/A	1.129	0.052	1.203	0.269	1.162	0.072	1.211	0.178
AAR3	N/A	2.544	0.441	2.230	0.428	2.583	0.355	2.200	0.554
OLE1	N/A	2.897	0.191	2.606	0.535	2.795	0.324	2.446	0.238
OLE2	N/A	2.764	0.450	1.913	0.816	2.673	0.563	1.737	0.342
TRP1	N/A	1.193	0.222	0.765	0.236	1.185	0.236	0.764	0.159
BALD	-0.610	-0.345	0.122	-2.075	1.456	-0.413	0.120	-2.020	0.819

Table A3: 1-hr and 8-hr relative MIR-3D and MOIR-3D reactivity metrics for July 2010.

Species	MIR	MIR-3D		MOIR-3D		MIR-3D-8hr		MOIR-3D-8hr	
		mean	stdev	mean	stdev	mean	stdev	mean	stdev
2MBT	14.450	4.279	1.438	2.097	2.716	3.682	1.063	2.907	2.552
BUTD	13.580	3.959	0.793	3.734	2.729	3.833	0.563	4.890	1.630
PRPE	11.580	3.720	0.746	4.071	3.157	3.577	0.484	5.413	2.312
ISOP	10.690	3.321	0.671	2.876	1.962	3.464	0.604	3.737	1.193
XYLM	10.610	3.219	0.748	1.882	1.198	2.855	0.382	2.687	0.886
ETHE	9.080	3.264	0.388	4.551	3.600	3.640	0.451	6.284	2.479
HCHO	8.970	4.423	1.424	3.791	3.043	4.046	1.117	5.700	3.346
ACRO	7.610	1.949	0.865	1.427	1.991	1.683	0.551	1.189	3.036
124B	7.180	2.203	0.444	1.295	0.821	1.989	0.230	1.787	0.518
CCHO	6.840	2.181	0.445	2.644	2.414	2.115	0.463	2.787	2.720
APIN	4.290	1.181	0.260	0.356	0.774	1.102	0.192	0.350	0.857
XYLP	4.250	1.369	0.121	0.846	0.568	1.329	0.089	1.189	0.562
TOLU	3.970	1.263	0.154	0.682	0.529	1.278	0.114	1.006	0.399
MCPT	2.420	0.814	0.115	1.040	0.721	0.885	0.117	1.360	0.338
ETOH	1.690	0.960	0.234	1.525	1.268	1.077	0.189	1.996	0.890
IPNT	1.670	0.727	0.134	1.242	1.014	0.814	0.131	1.680	0.647
N_C5	1.540	0.694	0.146	1.147	0.925	0.779	0.141	1.527	0.508
MEK	1.480	0.540	0.089	0.640	0.524	0.566	0.086	0.920	0.507
224P	1.440	0.635	0.109	1.042	0.887	0.694	0.097	1.401	0.535
N_C4	1.330	0.566	0.125	0.963	0.783	0.630	0.125	1.296	0.494
C2H2	1.250	0.409	0.069	0.462	0.345	0.409	0.050	0.662	0.197
BACT	0.890	0.525	0.103	0.776	0.589	0.581	0.105	1.062	0.366
C6H6	0.820	0.310	0.058	0.351	0.232	0.335	0.043	0.457	0.090
MTBE	0.780	0.493	0.100	0.880	0.764	0.546	0.090	1.175	0.471
MEOH	0.710	0.640	0.132	1.080	0.853	0.709	0.095	1.394	0.497
IPOH	0.710	0.516	0.084	0.932	0.836	0.566	0.088	1.225	0.552
DODC	0.660	0.296	0.091	0.057	0.343	0.318	0.041	0.041	0.451
ACET	0.430	0.173	0.027	0.215	0.170	0.180	0.021	0.302	0.139
C2H6	0.310	0.133	0.036	0.244	0.208	0.148	0.039	0.332	0.151
CO	0.060	0.071	0.019	0.153	0.141	0.084	0.018	0.192	0.080
CH4	0.010	0.007	0.002	0.014	0.012	0.008	0.001	0.018	0.008
RCHO	N/A	2.475	0.733	2.197	2.152	2.215	0.492	2.568	2.540
AAR1	N/A	0.616	0.152	1.136	0.950	0.711	0.135	1.529	0.606
AAR2	N/A	0.682	0.151	1.175	0.973	0.785	0.132	1.573	0.583
ALK3	N/A	0.678	0.123	0.645	0.448	0.739	0.084	0.875	0.264
ARO1	N/A	1.162	0.074	0.702	0.489	1.143	0.081	1.004	0.380
AAR3	N/A	2.448	0.308	1.540	0.981	2.391	0.296	2.218	0.618
OLE1	N/A	2.713	0.354	2.902	2.139	2.867	0.318	3.931	1.280
OLE2	N/A	2.448	0.508	1.434	1.465	2.456	0.561	1.721	1.315
TRP1	N/A	1.142	0.271	0.420	0.601	1.084	0.293	0.365	0.691
BALD	-0.610	-0.872	0.610	-4.913	5.918	-1.110	0.688	-7.005	5.204

Table A4: 1-hr and 8-hr relative MIR-3D and MOIR-3D reactivity metrics for May 2010.

		mean	stdev	mean	stdev	mean	stdev	mean	stdev
2MBT	14.450	3.650	0.798	9.030	8.697	3.875	0.851	4.093	1.774
BUTD	13.580	3.834	0.334	0.837	7.646	3.900	0.433	3.103	0.813
PRPE	11.580	3.752	0.237	12.664	16.333	3.640	0.315	4.540	0.954
ISOP	10.690	3.249	0.550	-3.941	15.086	3.362	0.414	2.149	1.168
XYLM	10.610	3.318	0.635	10.262	15.508	3.378	0.542	3.772	1.734
ETHE	9.080	3.457	0.267	39.314	72.258	3.536	0.276	8.247	4.517
HCHO	8.970	4.773	0.194	49.642	90.786	5.037	1.264	9.386	6.892
ACRO	7.610	1.926	0.388	-27.239	57.536	1.816	0.338	-1.994 3	4.196
124B	7.180	2.207	0.347	1.106	1.705	2.265	0.318	1.822.	

Table A5: 1-hr and 8-hr relative LS-RR reactivity metrics for July 1995.

		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	2.018	0.053	0.744	2.196	0.055	0.818
BUTD	13.580	2.794	0.036	0.930	2.932	0.038	0.953
PRPE	11.580	2.545	0.038	0.899	2.634	0.044	0.923
ISOP	10.690	2.594	0.037	0.920	2.760	0.040	0.951
XYLM	10.610	2.056	0.027	0.924	2.160	0.026	0.954
ETHE	9.080	2.920	0.045	0.905	2.950	0.046	0.931
HCHO	8.970	2.435	0.056	0.793	2.662	0.068	0.840
ACRO	7.610	1.675	0.042	0.795	1.609	0.043	0.843
124B	7.180	1.533	0.016	0.947	1.607	0.016	0.969
CCHO	6.840	1.904	0.050	0.784	1.881	0.052	0.849
APIN	4.290	0.898	0.014	0.907	0.951	0.014	0.951
XYLP	4.250	1.200	0.011	0.957	1.228	0.009	0.980
TOLU	3.970	1.275	0.011	0.962	1.285	0.010	0.980
MCPT	2.420	0.987	0.009	0.972	0.962	0.009	0.979
ETOH	1.690	1.183	0.016	0.936	1.124	0.014	0.960
IPNT	1.670	0.822	0.009	0.954	0.793	0.009	0.965
N_C5	1.540	0.890	0.010	0.954	0.858	0.011	0.963
MEK	1.480	0.632	0.009	0.924	0.605	0.009	0.948
224P	1.440	0.711	0.008	0.955	0.686	0.009	0.961
N_C4	1.330	0.708	0.009	0.946	0.678	0.009	0.959
C2H2	1.250	0.412	0.004	0.966	0.392	0.004	0.979
BACT	0.890	0.672	0.008	0.955	0.646	0.008	0.965
C6H6	0.820	0.423	0.004	0.975	0.409	0.004	0.975
MTBE	0.780	0.560	0.008	0.933	0.543	0.008	0.944
MEOH	0.710	0.720	0.010	0.924	0.692	0.010	0.939
IPOH	0.710	0.473	0.009	0.885	0.469	0.009	0.909
DODC	0.660	0.491	0.007	0.941	0.497	0.007	0.953
ACET	0.430	0.191	0.002	0.946	0.182	0.002	0.962
C2H6	0.310	0.176	0.003	0.908	0.165	0.003	0.928
CO	0.060	0.082	0.002	0.833	0.080	0.002	0.864
CH4	0.010	0.008	0.000	0.891	0.008	0.000	0.901
RCHO	N/A	1.860	0.040	0.831	1.829	0.039	0.894
AAR1	N/A	0.759	0.010	0.942	0.730	0.010	0.955
AAR2	N/A	0.830	0.009	0.955	0.808	0.009	0.967
ALK3	N/A	0.898	0.009	0.965	0.893	0.010	0.972
ARO1	N/A	1.155	0.010	0.967	1.148	0.009	0.983
AAR3	N/A	1.769	0.021	0.938	1.880	0.024	0.962
OLE1	N/A	2.249	0.028	0.937	2.336	0.031	0.959
OLE2	N/A	1.801	0.030	0.892	1.913	0.030	0.943
TRP1	N/A	0.881	0.010	0.938	0.934	0.011	0.969
BALD	-0.610	0.109	0.054	0.058	0.142	0.055	0.067

Table A6: 1-hr and 8-hr relative LS-RR reactivity metrics for May 1995.

		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	3.393	0.056	0.892	3.814	0.061	0.901
BUTD	13.580	3.295	0.024	0.978	3.386	0.022	0.984
PRPE	11.580	3.249	0.024	0.975	3.260	0.024	0.980
ISOP	10.690	2.991	0.025	0.974	3.107	0.022	0.983
XYLM	10.610	2.908	0.022	0.975	2.931	0.020	0.983
ETHE	9.080	3.615	0.035	0.967	3.523	0.037	0.969
HCHO	8.970	4.535	0.072	0.899	4.575	0.071	0.916
ACRO	7.610	1.488	0.030	0.808	1.436	0.035	0.786
124B	7.180	1.923	0.012	0.983	1.941	0.010	0.989
CCHO	6.840	1.781	0.031	0.869	1.726	0.034	0.867
APIN	4.290	1.058	0.013	0.938	1.167	0.012	0.967
XYLP	4.250	1.308	0.006	0.991	1.294	0.006	0.994
TOLU	3.970	1.386	0.006	0.992	1.369	0.006	0.994
MCPT	2.420	0.723	0.007	0.951	0.714	0.006	0.968
ETOH	1.690	0.978	0.010	0.957	0.968	0.009	0.972
IPNT	1.670	0.650	0.007	0.952	0.644	0.006	0.971
N_C5	1.540	0.634	0.007	0.944	0.624	0.006	0.968
MEK	1.480	0.554	0.005	0.969	0.545	0.004	0.978
224P	1.440	0.613	0.007	0.947	0.603	0.007	0.966
N_C4	1.330	0.506	0.006	0.946	0.500	0.005	0.969
C2H2	1.250	0.463	0.005	0.946	0.460	0.006	0.956
BACT	0.890	0.472	0.005	0.941	0.465	0.004	0.963
C6H6	0.820	0.332	0.003	0.967	0.327	0.002	0.981
MTBE	0.780	0.471	0.006	0.929	0.463	0.006	0.951
MEOH	0.710	0.696	0.011	0.915	0.689	0.011	0.931
IPOH	0.710	0.468	0.007	0.924	0.467	0.007	0.939
DODC	0.660	0.294	0.006	0.806	0.289	0.006	0.817
ACET	0.430	0.199	0.002	0.970	0.194	0.002	0.973
C2H6	0.310	0.110	0.002	0.927	0.110	0.001	0.958
CO	0.060	0.064	0.002	0.814	0.065	0.001	0.870
CH4	0.010	0.006	0.000	0.864	0.006	0.000	0.905
RCHO	N/A	1.869	0.027	0.899	1.857	0.028	0.918
AAR1	N/A	0.578	0.007	0.949	0.572	0.006	0.970
AAR2	N/A	0.627	0.006	0.960	0.619	0.005	0.978
ALK3	N/A	0.636	0.007	0.930	0.627	0.006	0.951
ARO1	N/A	1.227	0.005	0.992	1.209	0.005	0.994
AAR3	N/A	2.318	0.016	0.981	2.341	0.013	0.989
OLE1	N/A	2.508	0.016	0.984	2.516	0.014	0.988
OLE2	N/A	2.163	0.023	0.952	2.324	0.021	0.974
TRP1	N/A	0.968	0.009	0.963	1.073	0.010	0.974
BALD	-0.610	-0.266	0.031	0.266	-0.289	0.038	0.315

Table A7: 1-hr and 8-hr relative LS-RR reactivity metrics for July 2010.

		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	2.426	0.173	0.639	2.525	0.155	0.688
BUTD	13.580	3.043	0.084	0.884	3.217	0.084	0.915
PRPE	11.580	3.016	0.092	0.872	3.141	0.093	0.897
ISOP	10.690	2.663	0.081	0.860	2.901	0.082	0.902
XYLM	10.610	2.453	0.064	0.900	2.606	0.064	0.933
ETHE	9.080	3.431	0.183	0.777	3.408	0.139	0.833
HCHO	8.970	3.279	0.159	0.754	3.657	0.167	0.783
ACRO	7.610	1.424	0.126	0.551	1.270	0.162	0.465
124B	7.180	1.712	0.038	0.924	1.808	0.038	0.949
CCHO	6.840	1.738	0.120	0.642	1.597	0.149	0.577
APIN	4.290	0.845	0.035	0.792	0.926	0.035	0.835
XYLP	4.250	1.295	0.027	0.940	1.333	0.029	0.949
TOLU	3.970	1.324	0.023	0.961	1.333	0.024	0.964
MCPT	2.420	0.920	0.020	0.947	0.900	0.023	0.939
ETOH	1.690	1.092	0.041	0.859	1.037	0.045	0.845
IPNT	1.670	0.816	0.026	0.900	0.787	0.028	0.887
N_C5	1.540	0.820	0.025	0.908	0.794	0.027	0.901
MEK	1.480	0.563	0.024	0.824	0.534	0.028	0.791
224P	1.440	0.731	0.022	0.903	0.707	0.023	0.901
N_C4	1.330	0.647	0.021	0.893	0.615	0.024	0.871
C2H2	1.250	0.426	0.010	0.936	0.407	0.012	0.922
BACT	0.890	0.604	0.018	0.914	0.581	0.020	0.899
C6H6	0.820	0.377	0.008	0.943	0.368	0.008	0.959
MTBE	0.780	0.563	0.022	0.848	0.547	0.023	0.843
MEOH	0.710	0.726	0.029	0.839	0.688	0.030	0.826
IPOH	0.710	0.536	0.028	0.763	0.534	0.028	0.760
DODC	0.660	0.406	0.015	0.858	0.416	0.017	0.872
ACET	0.430	0.182	0.007	0.863	0.172	0.008	0.831
C2H6	0.310	0.150	0.007	0.824	0.140	0.008	0.789
CO	0.060	0.082	0.006	0.662	0.080	0.006	0.671
CH4	0.010	0.008	0.000	0.798	0.007	0.000	0.768
RCHO	N/A	1.713	0.102	0.685	1.659	0.126	0.636
AAR1	N/A	0.723	0.028	0.867	0.690	0.029	0.852
AAR2	N/A	0.794	0.026	0.901	0.770	0.026	0.895
ALK3	N/A	0.814	0.020	0.930	0.814	0.021	0.939
ARO1	N/A	1.202	0.022	0.954	1.208	0.021	0.966
AAR3	N/A	2.009	0.045	0.924	2.127	0.049	0.939
OLE1	N/A	2.421	0.065	0.897	2.535	0.063	0.923
OLE2	N/A	1.790	0.072	0.795	1.919	0.069	0.847
TRP1	N/A	0.831	0.029	0.828	0.917	0.030	0.881
BALD	-0.610	-0.318	0.178	0.114	-0.304	0.185	0.158

Table A8: 1-hr and 8-hr relative LS-RR reactivity metrics for May 2010.

		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	3.390	0.142	0.853	3.817	0.155	0.859
BUTD	13.580	3.422	0.083	0.957	3.393	0.049	0.978
PRPE	11.580	3.341	0.071	0.959	3.250	0.045	0.978
ISOP	10.690	3.071	0.097	0.947	3.141	0.055	0.975
XYLM	10.610	3.097	0.056	0.970	3.045	0.045	0.983
ETHE	9.080	3.619	0.118	0.942	3.422	0.120	0.932
HCHO	8.970	4.926	0.202	0.889	4.712	0.167	0.903
ACRO	7.610	1.433	0.101	0.747	1.478	0.103	0.715
124B	7.180	1.996	0.032	0.970	1.983	0.027	0.983
CCHO	6.840	1.802	0.128	0.782	1.751	0.126	0.747
APIN	4.290	1.029	0.034	0.940	1.155	0.032	0.958
XYLP	4.250	1.344	0.018	0.981	1.304	0.014	0.989
TOLU	3.970	1.429	0.016	0.991	1.386	0.013	0.993
MCPT	2.420	0.684	0.018	0.954	0.686	0.014	0.970
ETOH	1.690	0.844	0.029	0.904	0.907	0.022	0.955
IPNT	1.670	0.607	0.016	0.937	0.618	0.014	0.963
N_C5	1.540	0.575	0.016	0.944	0.586	0.011	0.972
MEK	1.480	0.512	0.013	0.947	0.530	0.011	0.968
224P	1.440	0.597	0.019	0.926	0.596	0.019	0.939
N_C4	1.330	0.452	0.012	0.928	0.470	0.010	0.968
C2H2	1.250	0.446	0.017	0.886	0.457	0.016	0.918
BACT	0.890	0.422	0.012	0.935	0.432	0.009	0.965
C6H6	0.820	0.319	0.007	0.965	0.320	0.006	0.979
MTBE	0.780	0.447	0.017	0.898	0.445	0.017	0.917
MEOH	0.710	0.657	0.035	0.789	0.679	0.037	0.830
IPOH	0.710	0.451	0.020	0.869	0.449	0.020	0.881
DODC	0.660	0.249	0.014	0.752	0.263	0.013	0.839
ACET	0.430	0.194	0.005	0.927	0.196	0.005	0.956
C2H6	0.310	0.094	0.003	0.880	0.101	0.003	0.949
CO	0.060	0.057	0.005	0.642	0.064	0.005	0.716
CH4	0.010	0.006	0.000	0.729	0.006	0.000	0.792
RCHO	N/A	1.776	0.093	0.844	1.813	0.095	0.839
AAR1	N/A	0.531	0.018	0.900	0.549	0.017	0.944
AAR2	N/A	0.574	0.014	0.942	0.588	0.011	0.972
ALK3	N/A	0.584	0.017	0.944	0.584	0.015	0.959
ARO1	N/A	1.250	0.019	0.986	1.218	0.011	0.994
AAR3	N/A	2.456	0.045	0.976	2.416	0.034	0.987
OLE1	N/A	2.500	0.045	0.971	2.474	0.030	0.985
OLE2	N/A	2.087	0.064	0.936	2.285	0.052	0.959
TRP1	N/A	0.934	0.024	0.955	1.054	0.029	0.957
BALD	-0.610	-0.106	0.107	0.269	-0.119	0.093	0.351

Table A9: 1-hr and 8-hr relative LS-RR reactivity metrics for July 1995 (no-intercept).

		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	2.136	0.059	0.682	2.273	0.063	0.743
BUTD	13.580	3.140	0.045	0.866	3.232	0.047	0.911
PRPE	11.580	3.030	0.052	0.748	3.085	0.057	0.799
ISOP	10.690	2.558	0.041	0.908	2.652	0.047	0.942
XYLM	10.610	1.949	0.029	0.918	2.008	0.030	0.943
ETHE	9.080	3.940	0.081	0.600	3.956	0.086	0.637
HCHO	8.970	2.716	0.068	0.631	2.841	0.080	0.726
ACRO	7.610	1.691	0.043	0.782	1.680	0.046	0.819
124B	7.180	1.440	0.018	0.937	1.482	0.020	0.955
CCHO	6.840	2.126	0.056	0.701	2.132	0.063	0.711
APIN	4.290	0.806	0.016	0.888	0.842	0.018	0.927
XYLP	4.250	1.069	0.015	0.920	1.074	0.015	0.934
TOLU	3.970	1.042	0.019	0.869	1.037	0.021	0.882
MCPT	2.420	1.233	0.019	0.859	1.236	0.023	0.827
ETOH	1.690	1.568	0.030	0.697	1.565	0.035	0.615
IPNT	1.670	1.181	0.026	0.613	1.183	0.031	0.528
N_C5	1.540	1.220	0.025	0.723	1.222	0.030	0.655
MEK	1.480	0.776	0.014	0.794	0.776	0.016	0.748
224P	1.440	0.976	0.020	0.707	0.972	0.024	0.654
N_C4	1.330	1.000	0.022	0.658	1.002	0.026	0.562
C2H2	1.250	0.507	0.007	0.800	0.501	0.009	0.775
BACT	0.890	0.899	0.017	0.754	0.901	0.021	0.688
C6H6	0.820	0.436	0.004	0.966	0.429	0.006	0.958
MTBE	0.780	0.823	0.019	0.576	0.823	0.023	0.514
MEOH	0.710	1.011	0.022	0.634	1.000	0.025	0.589
IPOH	0.710	0.736	0.019	0.344	0.739	0.022	0.326
DODC	0.660	0.505	0.007	0.930	0.509	0.007	0.946
ACET	0.430	0.235	0.004	0.805	0.232	0.004	0.742
C2H6	0.310	0.260	0.006	0.555	0.260	0.008	0.394
CO	0.060	0.138	0.004	0.265	0.137	0.005	0.179
CH4	0.010	0.013	0.000	0.420	0.012	0.000	0.272
RCHO	N/A	2.206	0.048	0.720	2.233	0.051	0.719
AAR1	N/A	1.087	0.024	0.626	1.089	0.028	0.537
AAR2	N/A	1.140	0.023	0.702	1.145	0.027	0.645
ALK3	N/A	1.070	0.015	0.899	1.077	0.018	0.894
ARO1	N/A	1.005	0.014	0.915	0.993	0.015	0.927
AAR3	N/A	1.660	0.024	0.929	1.723	0.029	0.949
OLE1	N/A	2.636	0.042	0.808	2.699	0.045	0.844
OLE2	N/A	1.699	0.034	0.878	1.774	0.038	0.925
TRP1	N/A	0.802	0.012	0.923	0.834	0.015	0.947
BALD	-0.610	-2.320	0.165	-7.317	-2.434	0.193	-10.501

Table A10: 1-hr and 8-hr relative LS-RR reactivity metrics for May 1995 (no-intercept).

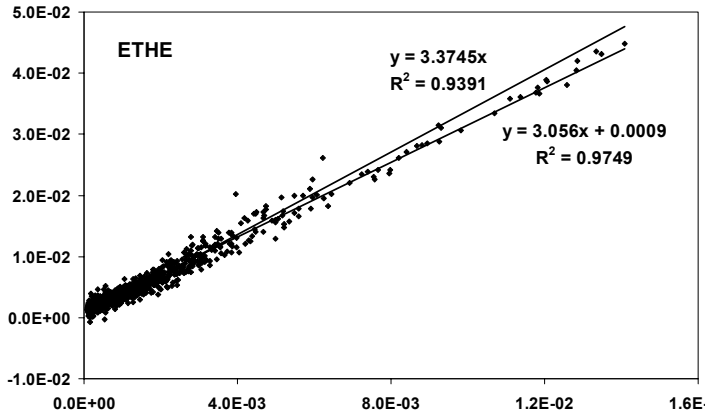
		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	3.317	0.057	0.889	3.673	0.064	0.897
BUTD	13.580	3.179	0.027	0.973	3.272	0.026	0.980
PRPE	11.580	3.383	0.026	0.971	3.446	0.029	0.973
ISOP	10.690	2.750	0.031	0.959	2.835	0.032	0.968
XYLM	10.610	2.973	0.026	0.968	3.031	0.024	0.977
ETHE	9.080	4.554	0.080	0.812	4.552	0.090	0.801
HCHO	8.970	5.109	0.087	0.867	5.282	0.091	0.876
ACRO	7.610	0.901	0.055	0.381	0.769	0.065	0.326
124B	7.180	1.852	0.013	0.979	1.886	0.012	0.987
CCHO	6.840	1.379	0.045	0.734	1.275	0.051	0.716
APIN	4.290	0.877	0.019	0.875	0.944	0.022	0.900
XYLP	4.250	1.286	0.007	0.989	1.285	0.006	0.992
TOLU	3.970	1.413	0.009	0.980	1.398	0.008	0.983
MCPT	2.420	0.708	0.010	0.894	0.710	0.009	0.911
ETOH	1.690	1.002	0.011	0.949	1.003	0.010	0.961
IPNT	1.670	0.757	0.011	0.892	0.767	0.012	0.902
N_C5	1.540	0.705	0.010	0.911	0.710	0.010	0.923
MEK	1.480	0.530	0.005	0.964	0.521	0.005	0.974
224P	1.440	0.766	0.014	0.800	0.767	0.015	0.823
N_C4	1.330	0.565	0.008	0.914	0.570	0.008	0.927
C2H2	1.250	0.570	0.010	0.774	0.564	0.010	0.805
BACT	0.890	0.482	0.007	0.899	0.483	0.006	0.915
C6H6	0.820	0.359	0.004	0.947	0.354	0.003	0.961
MTBE	0.780	0.611	0.012	0.725	0.614	0.013	0.749
MEOH	0.710	0.942	0.021	0.592	0.933	0.022	0.644
IPOH	0.710	0.643	0.015	0.595	0.657	0.017	0.623
DODC	0.660	0.211	0.009	0.062	0.201	0.009	0.022
ACET	0.430	0.217	0.002	0.933	0.211	0.002	0.941
C2H6	0.310	0.125	0.002	0.892	0.126	0.002	0.916
CO	0.060	0.099	0.003	0.166	0.101	0.003	0.312
CH4	0.010	0.009	0.000	0.426	0.009	0.000	0.519
RCHO	N/A	1.397	0.046	0.725	1.353	0.050	0.753
AAR1	N/A	0.703	0.012	0.848	0.709	0.012	0.863
AAR2	N/A	0.703	0.009	0.924	0.710	0.010	0.930
ALK3	N/A	0.591	0.011	0.806	0.589	0.009	0.830
ARO1	N/A	1.257	0.007	0.983	1.241	0.007	0.985
AAR3	N/A	2.310	0.017	0.977	2.358	0.015	0.986
OLE1	N/A	2.454	0.018	0.979	2.492	0.016	0.984
OLE2	N/A	1.859	0.033	0.910	1.961	0.037	0.928
TRP1	N/A	0.813	0.015	0.902	0.876	0.019	0.910
BALD	-0.610	-1.215	0.078	-5.001	-1.379	0.094	-5.402

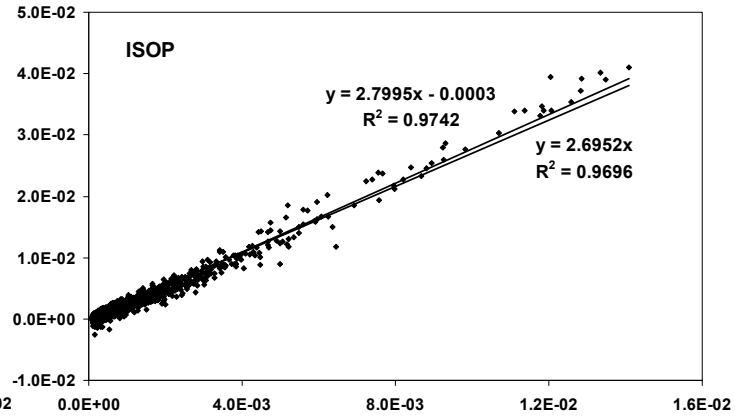
Table A11: 1-hr and 8-hr relative LS-RR reactivity metrics for July 2010 (no-intercept).

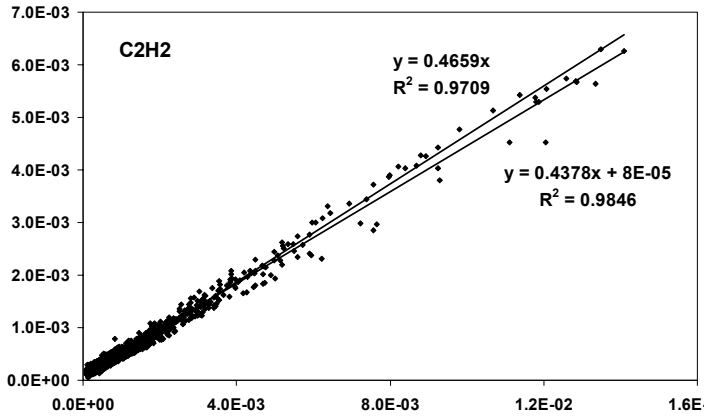
		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	2.636	0.183	0.590	2.946	0.185	0.564
BUTD	13.580	3.488	0.105	0.809	3.769	0.120	0.814
PRPE	11.580	3.771	0.138	0.719	4.068	0.161	0.678
ISOP	10.690	2.593	0.083	0.854	2.800	0.087	0.890
XYLM	10.610	2.485	0.065	0.896	2.664	0.066	0.926
ETHE	9.080	4.986	0.284	0.414	5.275	0.293	0.221
HCHO	8.970	3.899	0.184	0.661	4.454	0.217	0.620
ACRO	7.610	1.204	0.139	0.462	1.086	0.173	0.381
124B	7.180	1.675	0.041	0.918	1.775	0.040	0.944
CCHO	6.840	1.874	0.131	0.562	1.869	0.161	0.491
APIN	4.290	0.649	0.043	0.697	0.715	0.046	0.751
XYLP	4.250	1.218	0.032	0.924	1.225	0.035	0.927
TOLU	3.970	1.163	0.034	0.916	1.130	0.040	0.902
MCPT	2.420	1.147	0.037	0.791	1.176	0.044	0.745
ETOH	1.690	1.499	0.071	0.386	1.564	0.084	0.321
IPNT	1.670	1.226	0.061	0.284	1.289	0.074	0.026
N_C5	1.540	1.157	0.052	0.503	1.208	0.063	0.323
MEK	1.480	0.697	0.032	0.610	0.716	0.038	0.559
224P	1.440	1.053	0.049	0.449	1.092	0.058	0.243
N_C4	1.330	0.956	0.047	0.306	1.000	0.058	0.091
C2H2	1.250	0.559	0.022	0.610	0.577	0.027	0.412
BACT	0.890	0.821	0.034	0.569	0.855	0.042	0.439
C6H6	0.820	0.411	0.010	0.915	0.405	0.010	0.921
MTBE	0.780	0.873	0.048	0.204	0.924	0.057	-0.118
MEOH	0.710	1.094	0.059	0.144	1.145	0.070	-0.158
IPOH	0.710	0.885	0.055	0.010	0.957	0.064	-0.273
DODC	0.660	0.317	0.019	0.776	0.302	0.023	0.760
ACET	0.430	0.233	0.010	0.556	0.239	0.012	0.491
C2H6	0.310	0.236	0.014	-0.090	0.249	0.017	-0.223
CO	0.060	0.147	0.010	-0.277	0.159	0.012	-0.501
CH4	0.010	0.013	0.001	-0.449	0.014	0.001	-0.817
RCHO	N/A	1.935	0.115	0.587	2.022	0.143	0.496
AAR1	N/A	1.097	0.058	0.198	1.153	0.070	-0.029
AAR2	N/A	1.130	0.053	0.459	1.186	0.063	0.298
ALK3	N/A	0.911	0.025	0.893	0.929	0.027	0.891
ARO1	N/A	1.114	0.028	0.935	1.091	0.030	0.935
AAR3	N/A	1.987	0.046	0.921	2.123	0.050	0.934
OLE1	N/A	2.888	0.093	0.802	3.124	0.107	0.779
OLE2	N/A	1.580	0.079	0.768	1.713	0.077	0.824
TRP1	N/A	0.650	0.037	0.740	0.713	0.041	0.796
BALD	-0.610	-3.378	0.447	-6.685	-4.145	0.553	-6.045

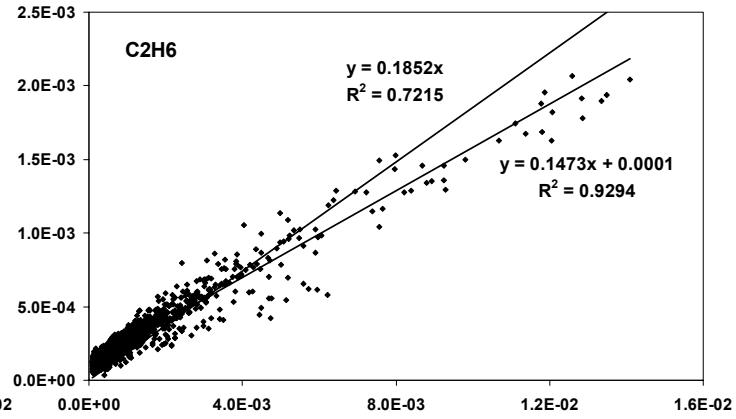
Table A12: 1-hr and 8-hr relative LS-RR reactivity metrics for May 2010 (no-intercept).

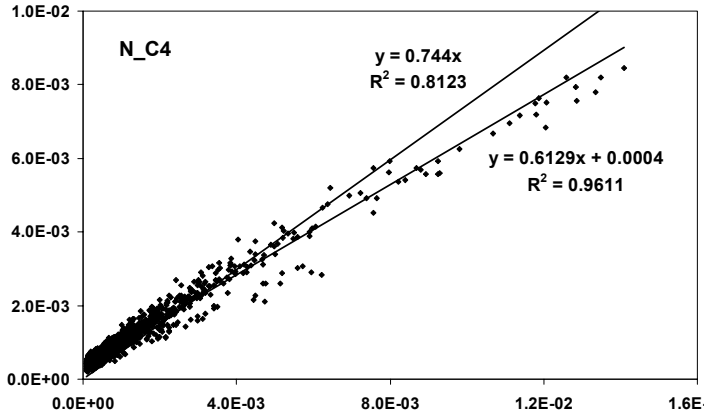
		1-hr			8-hr		
	MIR	LS-RR	Error	R^2	LS-RR	Error	R^2
2MBT	14.450	3.307	0.146	0.846	4.073	0.162	0.849
BUTD	13.580	3.429	0.089	0.952	3.475	0.061	0.973
PRPE	11.580	3.912	0.132	0.902	4.004	0.134	0.876
ISOP	10.690	2.758	0.116	0.928	2.798	0.085	0.954
XYLM	10.610	3.192	0.070	0.962	3.314	0.075	0.969
ETHE	9.080	5.739	0.402	0.365	5.806	0.400	0.190
HCHO	8.970	6.249	0.348	0.763	6.646	0.379	0.654
ACRO	7.610	0.096	0.301	-1.372	-0.153	0.317	-1.618
124B	7.180	1.874	0.038	0.962	1.914	0.028	0.979
CCHO	6.840	0.949	0.239	0.331	0.732	0.236	0.201
APIN	4.290	0.682	0.082	0.678	0.781	0.075	0.785
XYLP	4.250	1.307	0.024	0.970	1.284	0.019	0.979
TOLU	3.970	1.433	0.025	0.979	1.403	0.025	0.977
MCPT	2.420	0.685	0.025	0.903	0.677	0.022	0.903
ETOH	1.690	1.003	0.036	0.823	1.058	0.032	0.893
IPNT	1.670	0.891	0.049	0.556	0.916	0.047	0.619
N_C5	1.540	0.766	0.036	0.721	0.779	0.031	0.797
MEK	1.480	0.462	0.019	0.914	0.471	0.016	0.943
224P	1.440	0.950	0.063	0.359	0.964	0.059	0.410
N_C4	1.330	0.617	0.030	0.681	0.639	0.027	0.763
C2H2	1.250	0.673	0.042	0.488	0.694	0.040	0.529
BACT	0.890	0.473	0.016	0.868	0.477	0.014	0.895
C6H6	0.820	0.375	0.014	0.884	0.362	0.010	0.932
MTBE	0.780	0.777	0.059	0.000	0.789	0.055	0.100
MEOH	0.710	1.234	0.098	-0.223	1.264	0.093	-0.060
IPOH	0.710	0.877	0.077	-0.548	0.908	0.074	-0.519
DODC	0.660	0.079	0.039	-1.273	0.046	0.042	-1.830
ACET	0.430	0.232	0.007	0.861	0.235	0.007	0.900
C2H6	0.310	0.136	0.007	0.544	0.143	0.007	0.680
CO	0.060	0.146	0.015	-1.453	0.153	0.014	-1.103
CH4	0.010	0.012	0.001	-0.572	0.013	0.001	-0.368
RCHO	N/A	0.840	0.232	0.097	0.764	0.224	0.187
AAR1	N/A	0.850	0.055	0.308	0.877	0.052	0.430
AAR2	N/A	0.786	0.037	0.688	0.810	0.035	0.747
ALK3	N/A	0.512	0.028	0.828	0.491	0.029	0.769
ARO1	N/A	1.285	0.030	0.971	1.252	0.022	0.980
AAR3	N/A	2.423	0.048	0.972	2.494	0.043	0.981
OLE1	N/A	2.628	0.052	0.961	2.667	0.046	0.964
OLE2	N/A	1.577	0.125	0.802	1.755	0.108	0.874
TRP1	N/A	0.660	0.065	0.742	0.735	0.066	0.806
BALD	-0.610	-2.477	0.419	-8.900	-2.920	0.448	-14.242

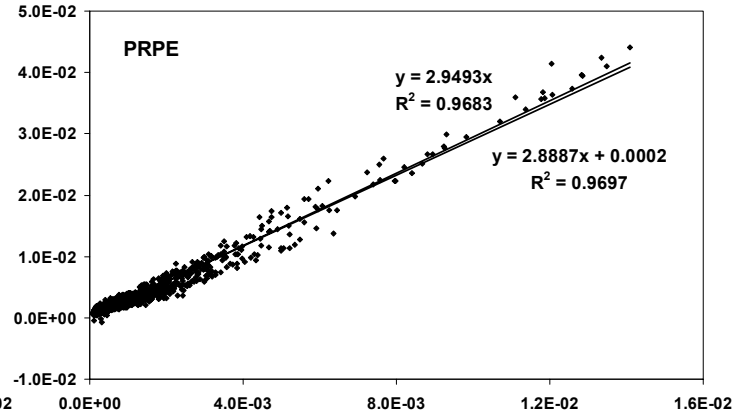

ETHE
y = 3.3745x
R2 = 0.9391
y = 3.056x + 0.0009
R2 = 0.9749
5.0E-02
4.0E-02
3.0E-02
2.0E-02
1.0E-02
0.0E+00
-1.0E-02
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

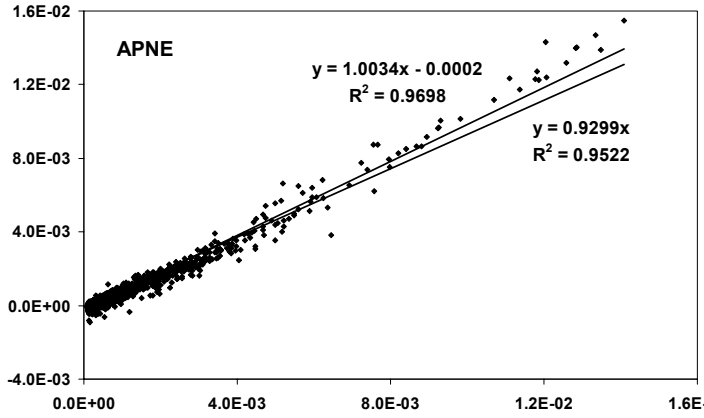

ISOP
y = 2.7995x - 0.0003
R2 = 0.9742
y = 2.6952x
R2 = 0.9696
5.0E-02
4.0E-02
3.0E-02
2.0E-02
1.0E-02
0.0E+00
-1.0E-02
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

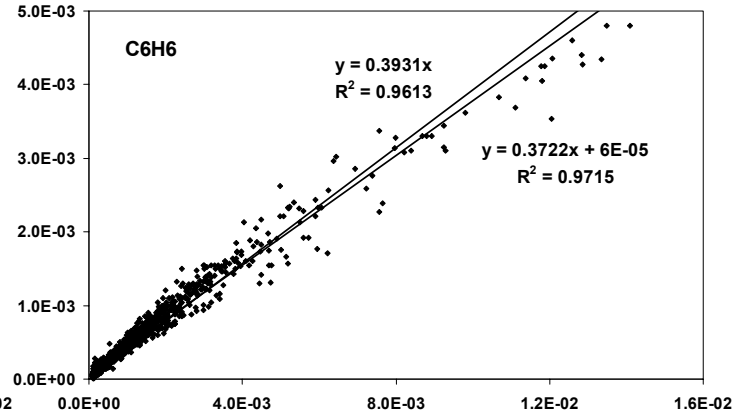

C2H2
y = 0.4659x
R2 = 0.9709
y = 0.4378x + 8E-05
R2 = 0.9846
7.0E-03
6.0E-03
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

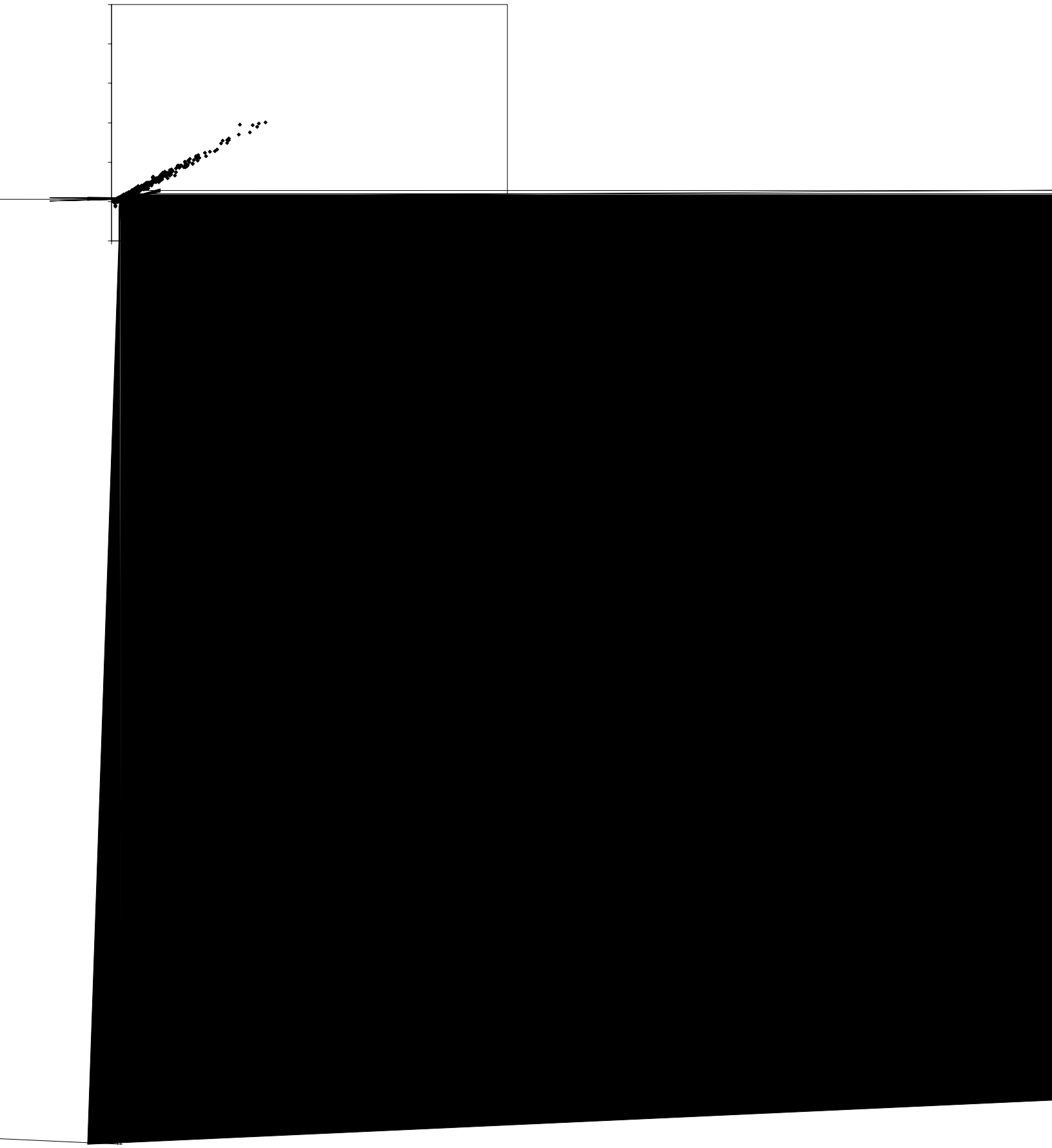

C2H6
y = 0.1852x
R2 = 0.7215
y = 0.1473x + 0.0001
R2 = 0.9294
2.5E-03
2.0E-03
1.5E-03
1.0E-03
5.0E-04
0.0E+00
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

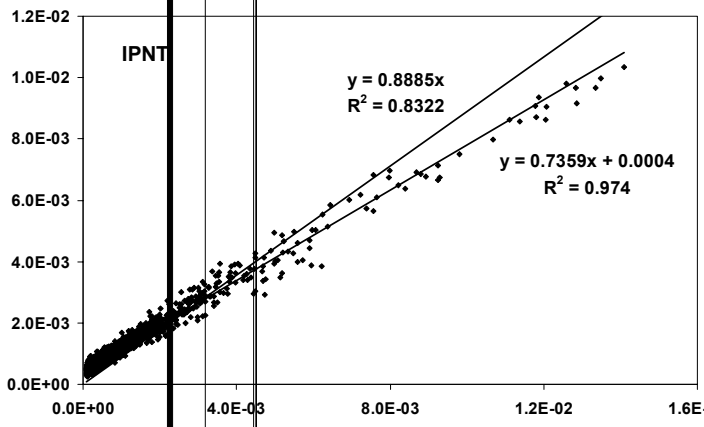

N_C4
y = 0.744x
R2 = 0.8123
y = 0.6129x + 0.0004
R2 = 0.9611
1.0E-02
8.0E-03
6.0E-03
4.0E-03
2.0E-03
0.0E+00
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

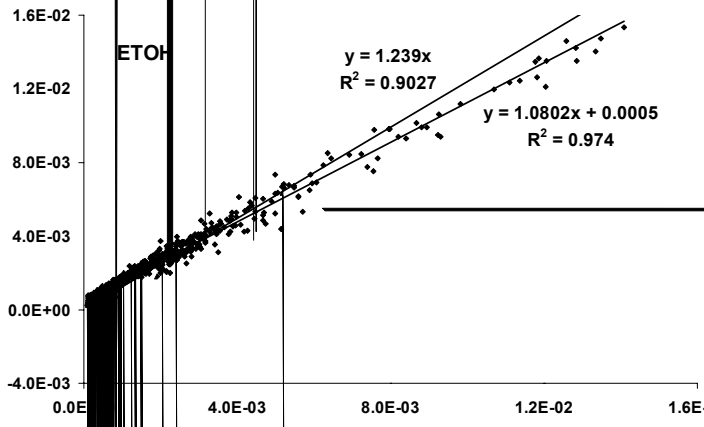

PRPE
y = 2.9493x
R2 = 0.9683
y = 2.8887x + 0.0002
R2 = 0.9697
5.0E-02
4.0E-02
3.0E-02
2.0E-02
1.0E-02
0.0E+00
-1.0E-02
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

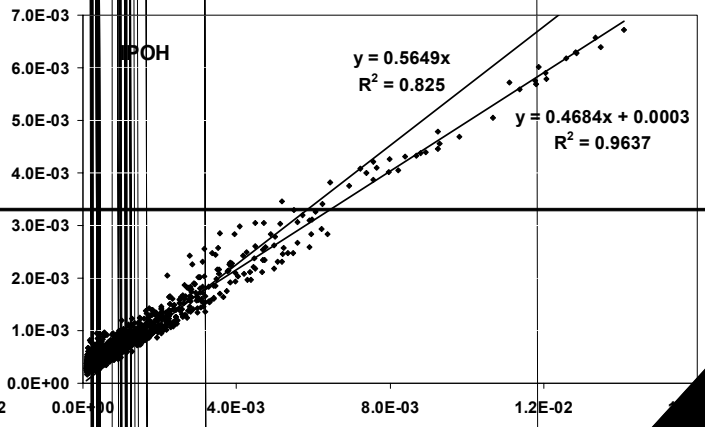

APNE
y = 1.0034x - 0.0002
R2 = 0.9698
y = 0.9299x
R2 = 0.9522
1.6E-02
1.2E-02
8.0E-03
4.0E-03
0.0E+00
-4.0E-03
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

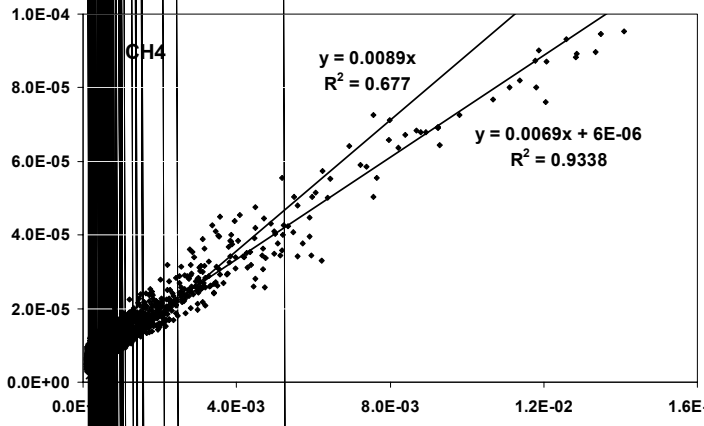

C6H6
y = 0.3931x
R2 = 0.9613
y = 0.3722x + 6E-05
R2 = 0.9715
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02

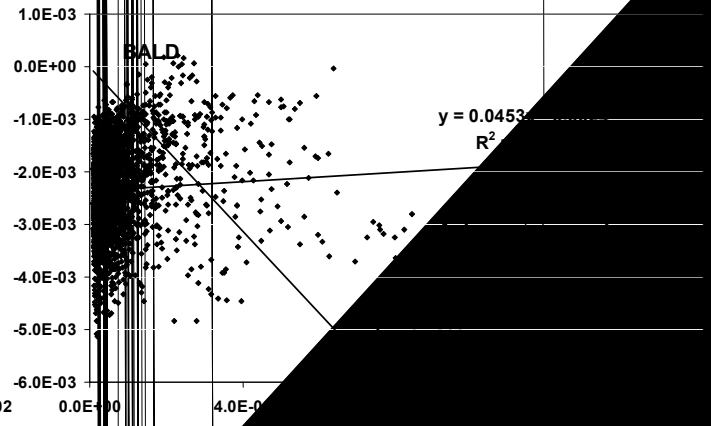


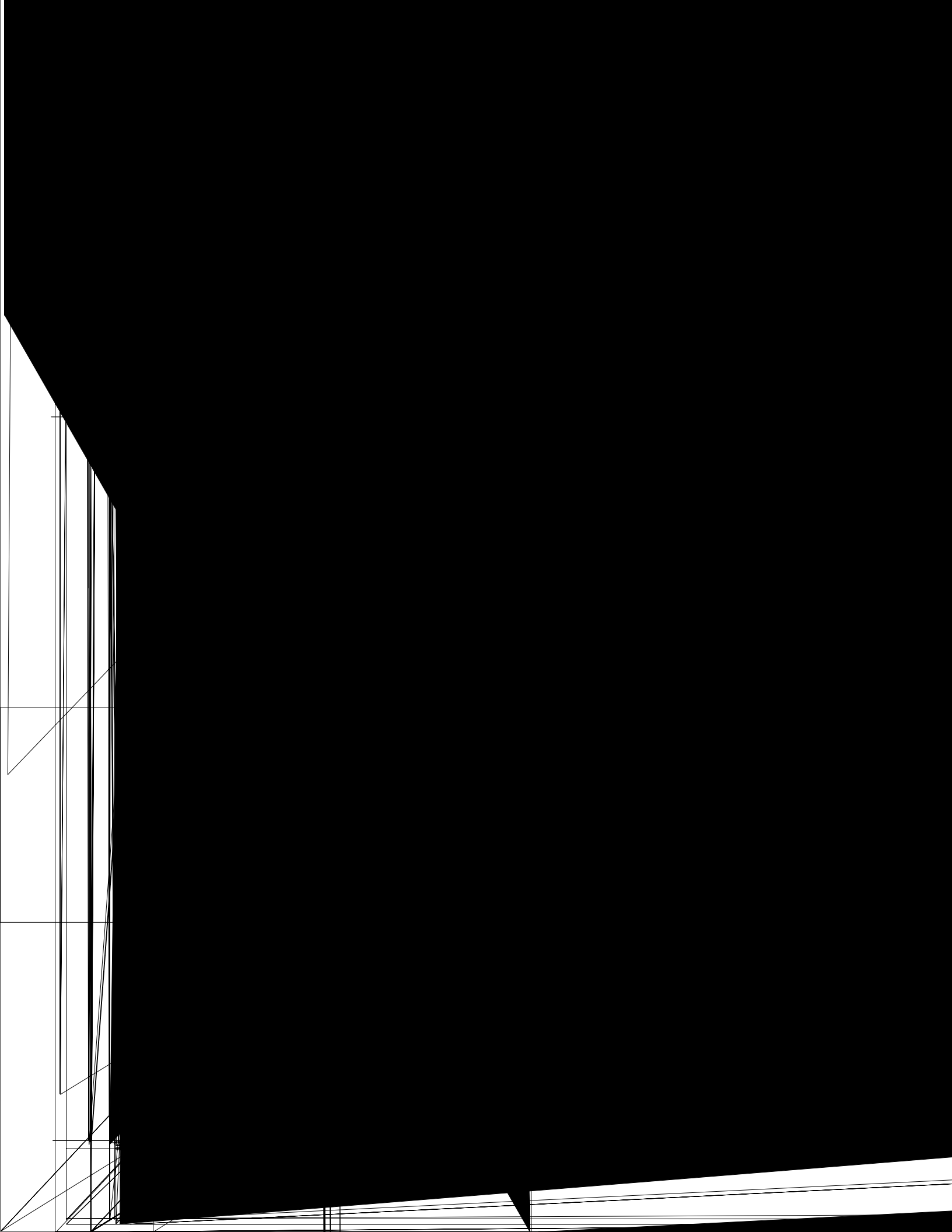

IPNT
y = 0.8885x
R2 = 0.8322
y = 0.7359x + 0.0004
R2 = 0.974
1.2E-02
1.0E-02
8.0E-03
6.0E-03
4.0E-03
2.0E-03
0.0E+00
0.0E+00
4.0E-03
8.0E-03
1.2E-02
1.6E-02


ETOH
y = 1.239x
R2 = 0.9027
y = 1.0802x + 0.0005
R2 = 0.974
1.6E-02
1.2E-02
8.0E-03
4.0E-03
0.0E+00
-4.0E-03
0.0E
4.0E-03
8.0E-03
1.2E-02
1.6E-02

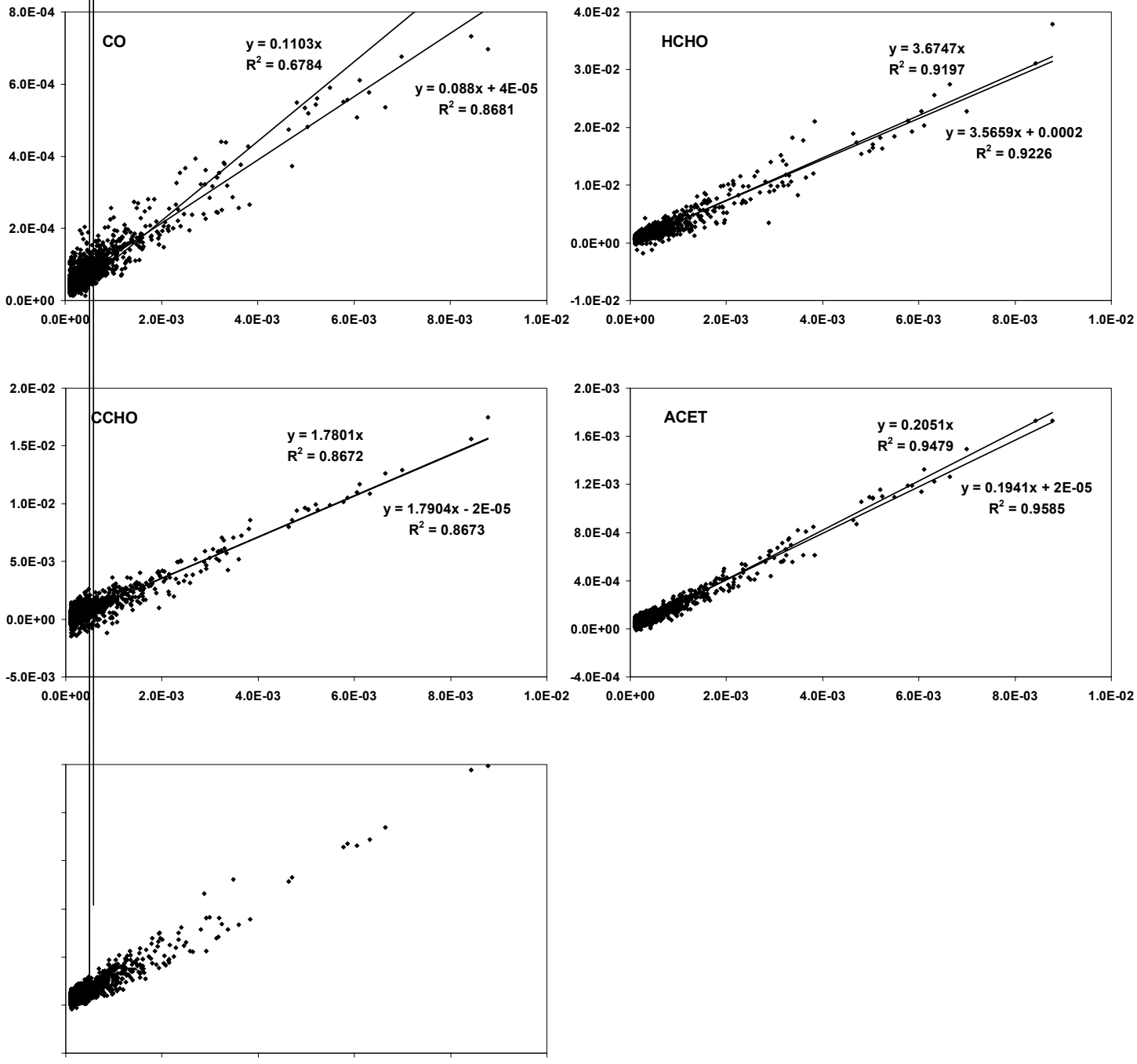

IPOH
y = 0.5649x
R2 = 0.825
y = 0.4684x + 0.0003
R2 = 0.9637
7.0E-03
6.0E-03
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
4.0E-03
8.0E-03
1.2E-02

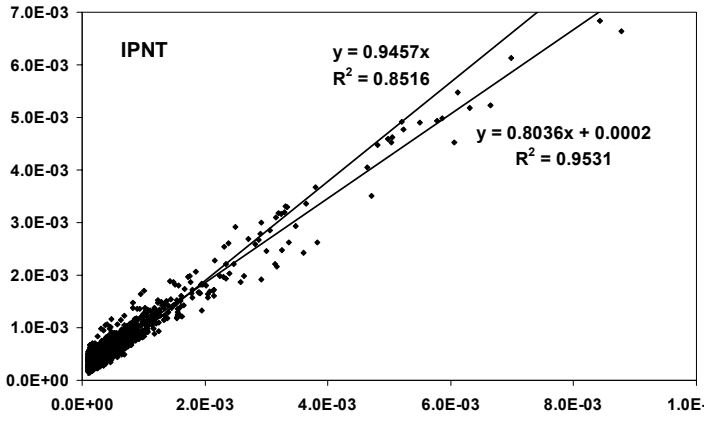

CH4
y = 0.0089x
R2 = 0.677
y = 0.0069x + 6E-06
R2 = 0.9338
1.0E-04
8.0E-05
6.0E-05
4.0E-05
2.0E-05
0.0E+00
0.0E
4.0E-03
8.0E-03
1.2E-02
1.6E-02

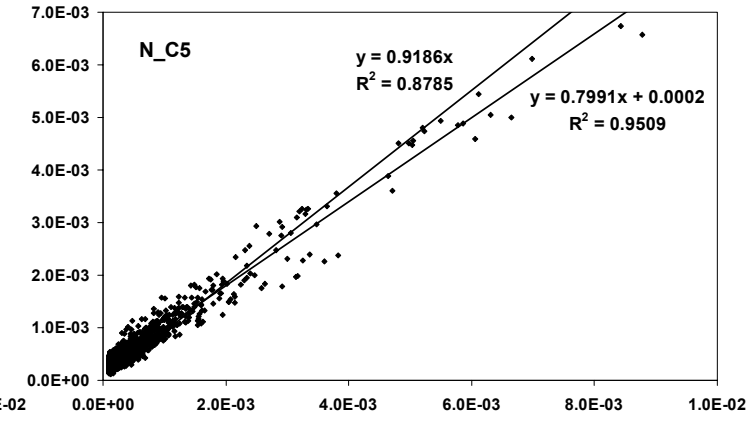

BALD
1.0E-03
0.0E+00
-1.0E-03
-2.0E-03
-3.0E-03
-4.0E-03
-5.0E-03
-6.0E-03
0.0E+00
4.0E-0

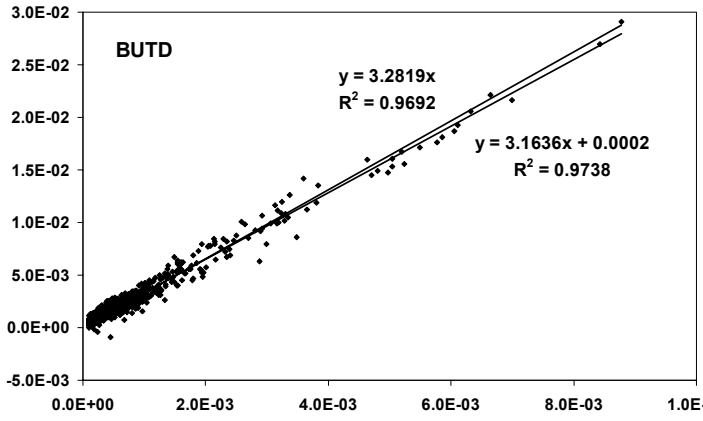


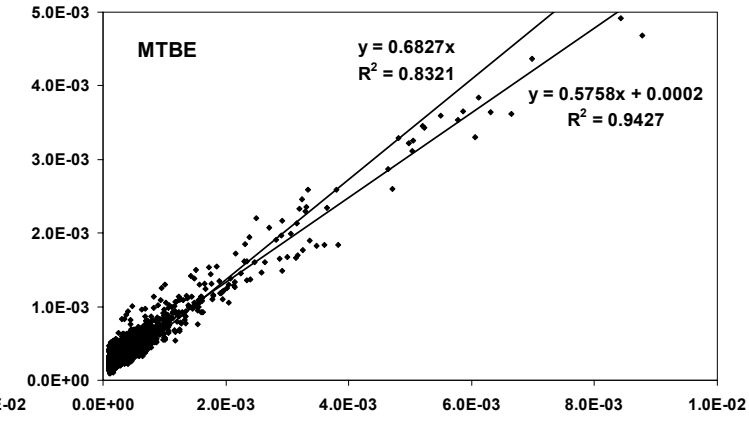
Appendix B2: July 2010.

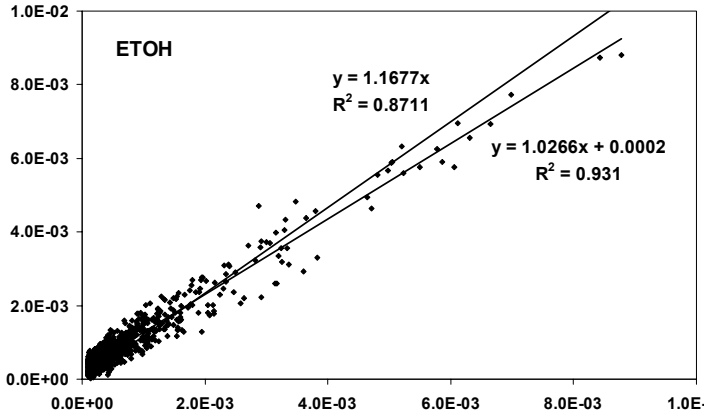


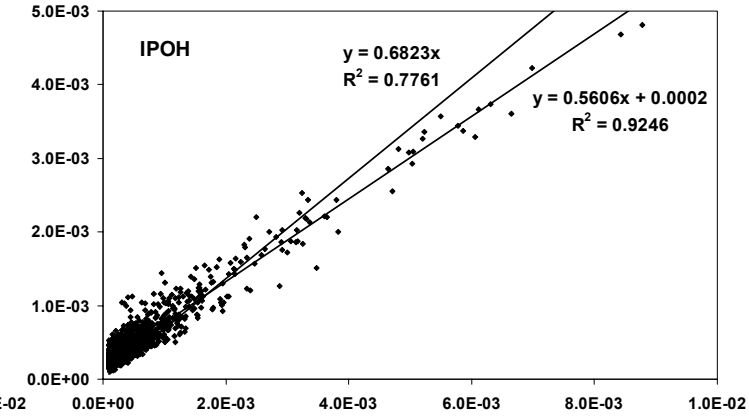

IPNT
y = 0.9457x
R2 = 0.8516
y = 0.8036x + 0.0002
R2 = 0.9531
7.0E-03
6.0E-03
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

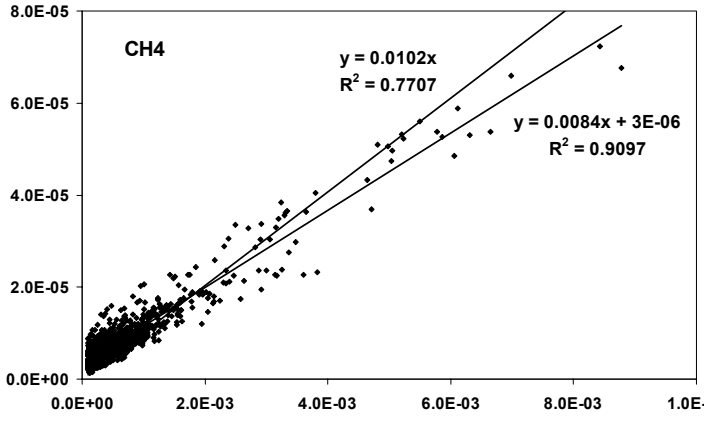

N_C5
y = 0.9186x
R2 = 0.8785
y = 0.7991x + 0.0002
R2 = 0.9509
7.0E-03
6.0E-03
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

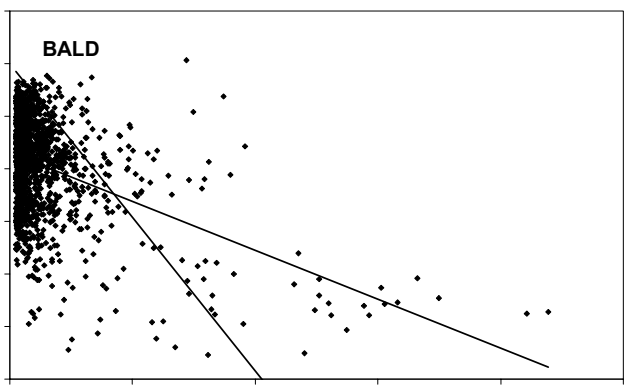

BUTD
y = 3.2819x
R2 = 0.9692
y = 3.1636x + 0.0002
R2 = 0.9738
3.0E-02
2.5E-02
2.0E-02
1.5E-02
1.0E-02
5.0E-03
0.0E+00
-5.0E-03
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

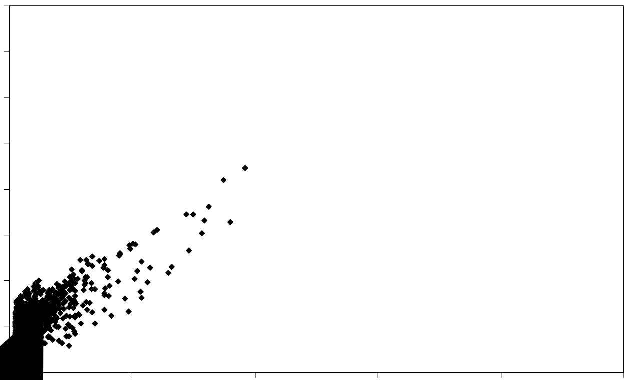

MTBE
y = 0.6827x
R2 = 0.8321
y = 0.5758x + 0.0002
R2 = 0.9427
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

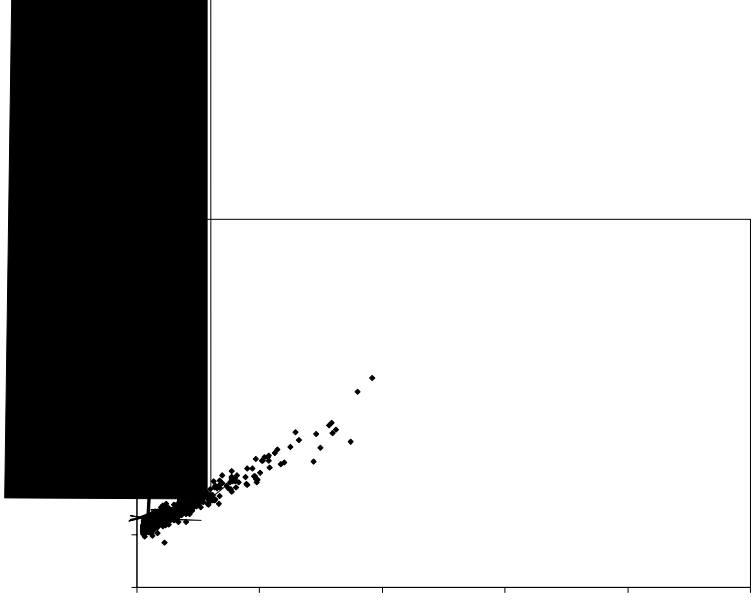

ETOH
y = 1.1677x
R2 = 0.8711
y = 1.0266x + 0.0002
R2 = 0.931
1.0E-02
8.0E-03
6.0E-03
4.0E-03
2.0E-03
0.0E+00
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

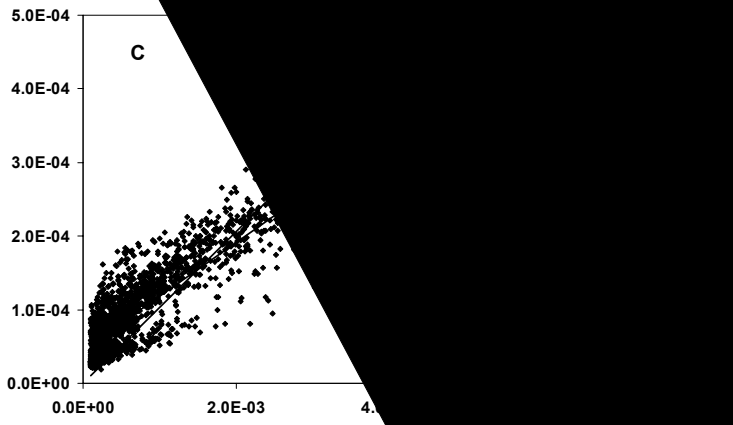

IPOH
y = 0.6823x
R2 = 0.7761
y = 0.5606x + 0.0002
R2 = 0.9246
5.0E-03
4.0E-03
3.0E-03
2.0E-03
1.0E-03
0.0E+00
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

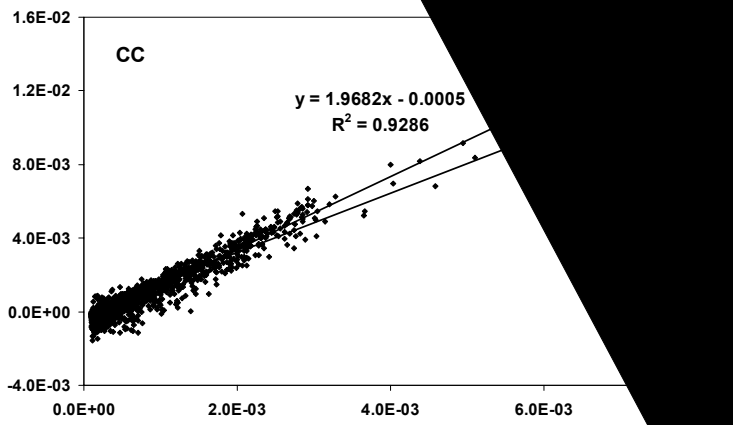

CH4
y = 0.0102x
R2 = 0.7707
y = 0.0084x + 3E-06
R2 = 0.9097
8.0E-05
6.0E-05
4.0E-05
2.0E-05
0.0E+00
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03
1.0E-02

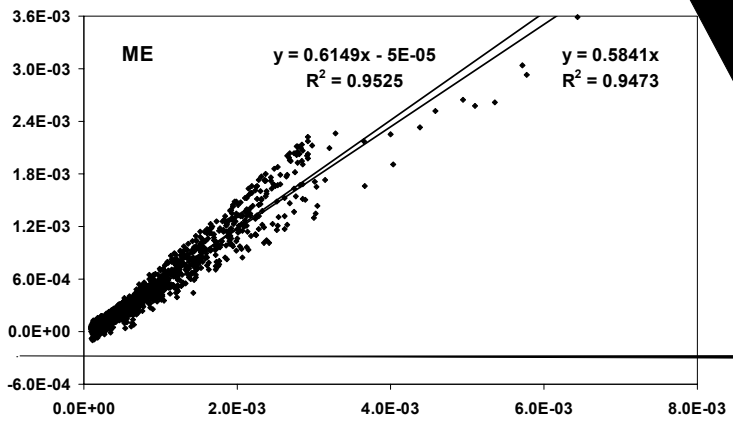

BALD






C
5.0E-04
4.0E-04
3.0E-04
2.0E-04
1.0E-04
0.0E+00
0.0E+00
2.0E-03


CC
y = 1.9682x - 0.0005
R2 = 0.9286
1.6E-02
1.2E-02
8.0E-03
4.0E-03
0.0E+00
-4.0E-03
0.0E+00
2.0E-03
4.0E-03
6.0E-03


ME
y = 0.6149x - 5E-05
R2 = 0.9525
y = 0.5841x
R2 = 0.9473
3.6E-03
3.0E-03
2.4E-03
1.8E-03
1.2E-03
6.0E-04
0.0E+00
-6.0E-04
0.0E+00
2.0E-03
4.0E-03
6.0E-03
8.0E-03

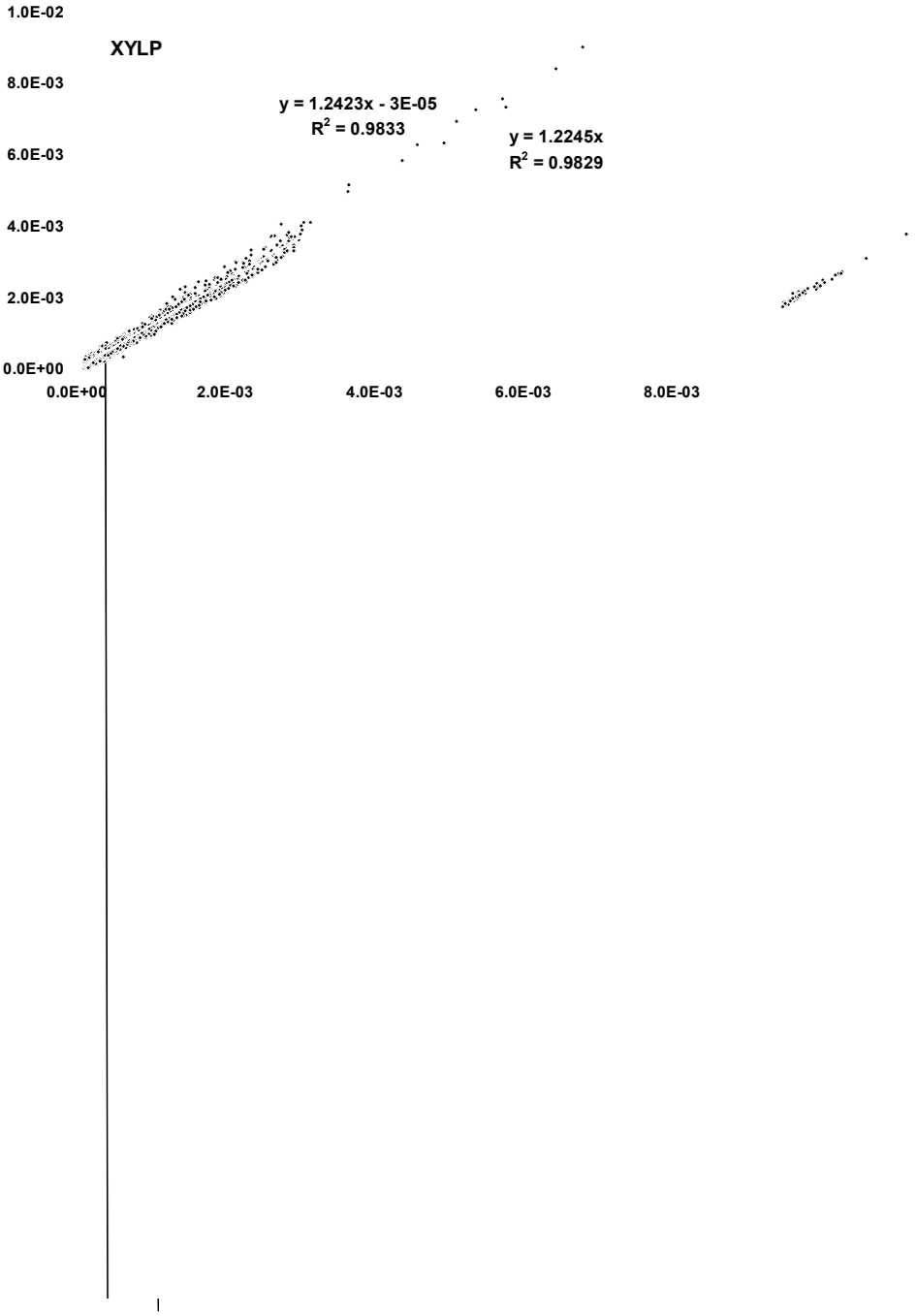

3.0E-02
ETHE
2.5E-02
2.0E-02
1.5E-02
1.0E-02
3.0E-03

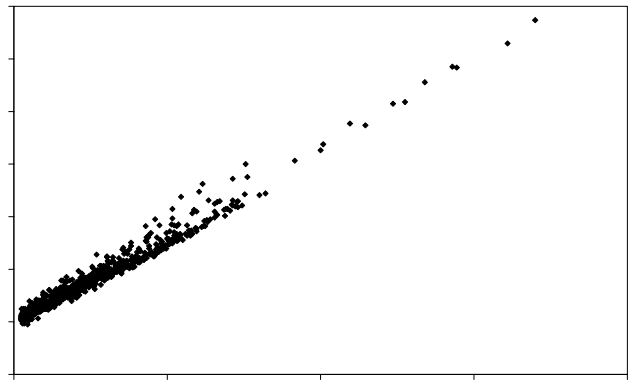
2.

LMy = 2.5009x + 0.0001

1.

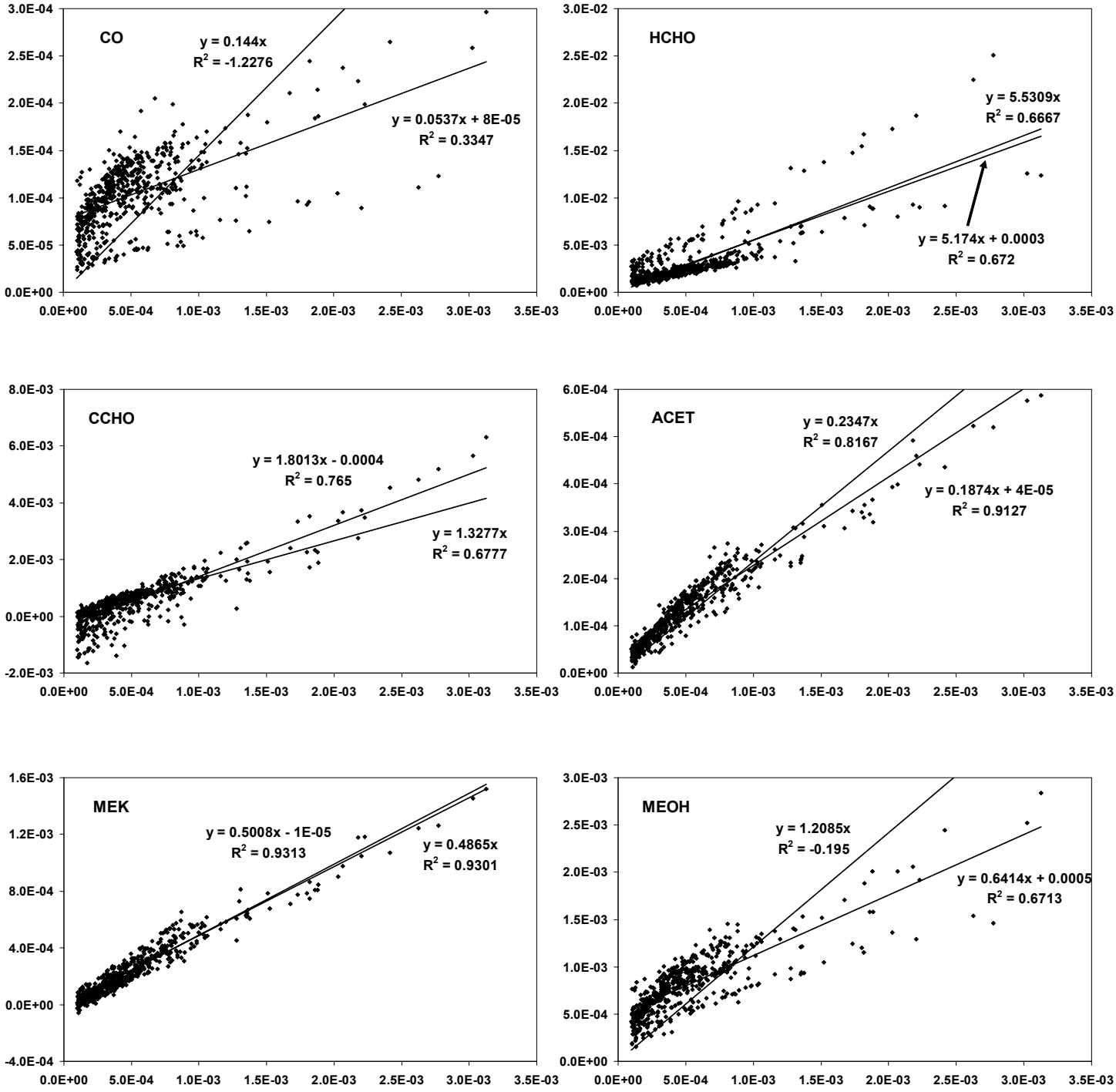
R2 = 0.91040.0E+004.0E-038.0E-031.2E-02

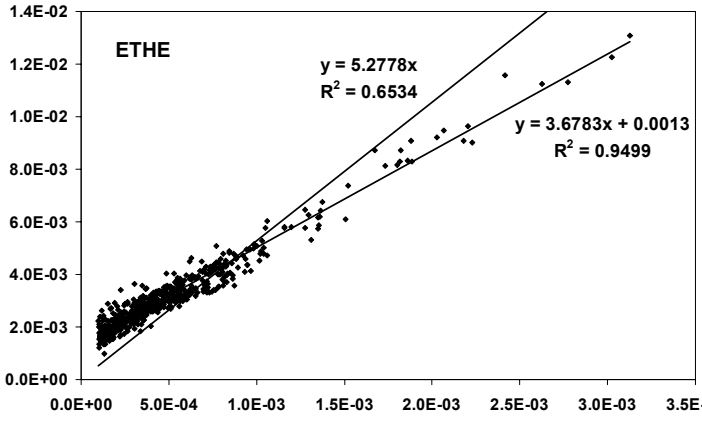


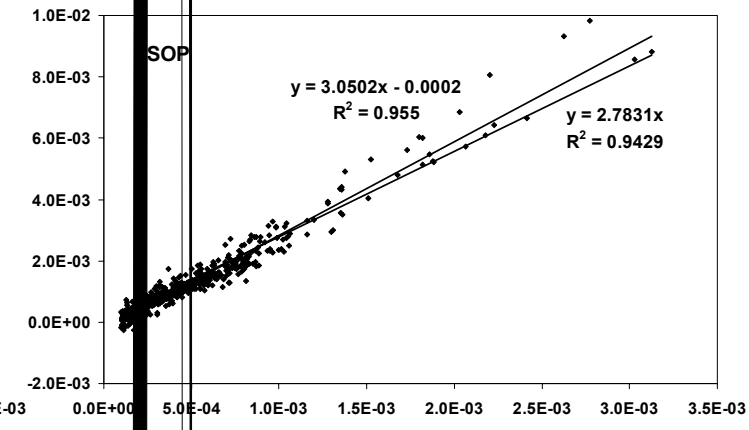


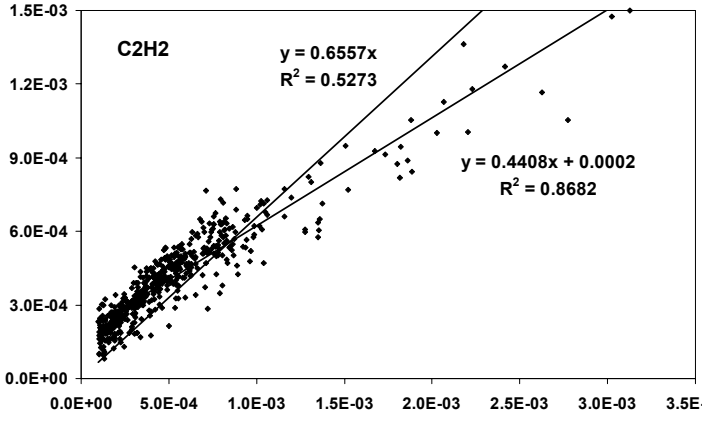

1.5E-02
1.2E-02
OLE2y = 2.0234x - 0.0003
R
3.0E-036.0E-039.0E-03
-3.0 -030.0E+00
0.0E 00
2.0E-03
4.0E-03
6.0E-03
8.0E-03

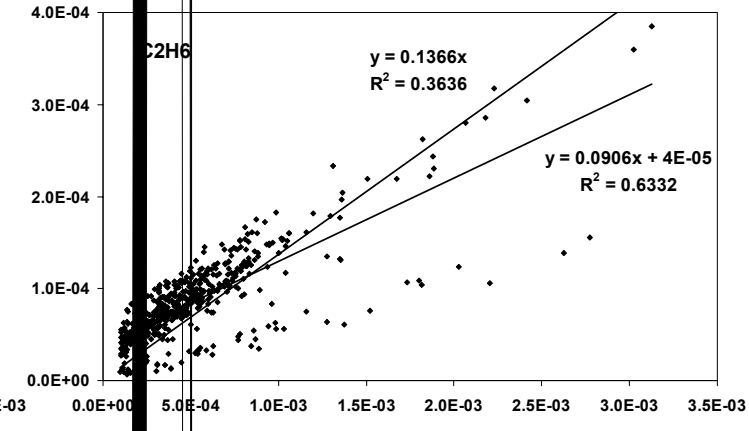
Appendix B4: May 2010.

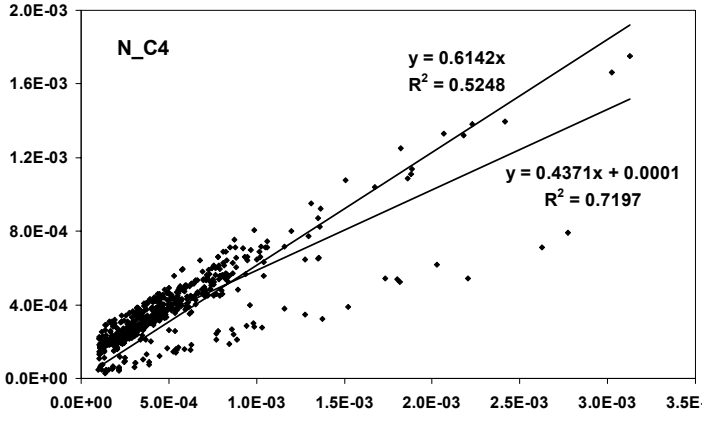


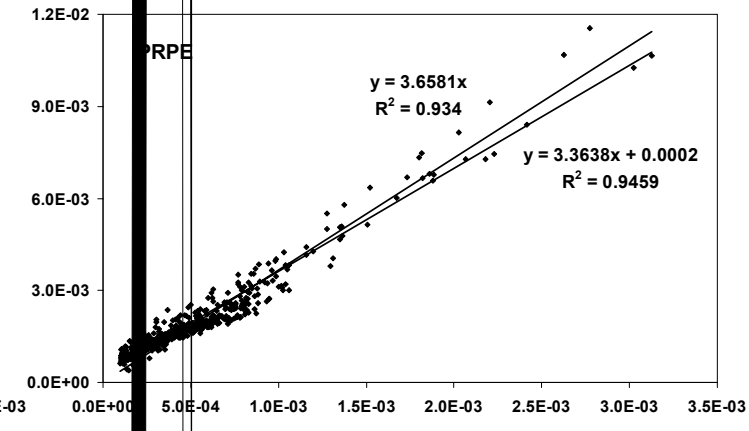

ETHE
y = 5.2778x
R2 = 0.6534
y = 3.6783x + 0.0013
R2 = 0.9499

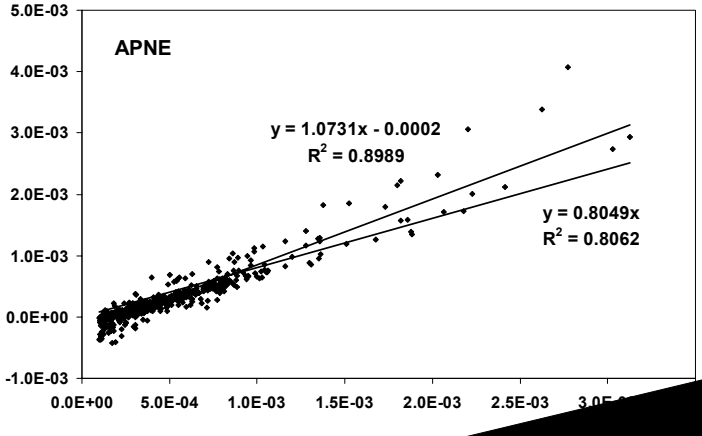

SOP
y = 3.0502x - 0.0002
R2 = 0.955
y = 2.7831x
R2 = 0.9429

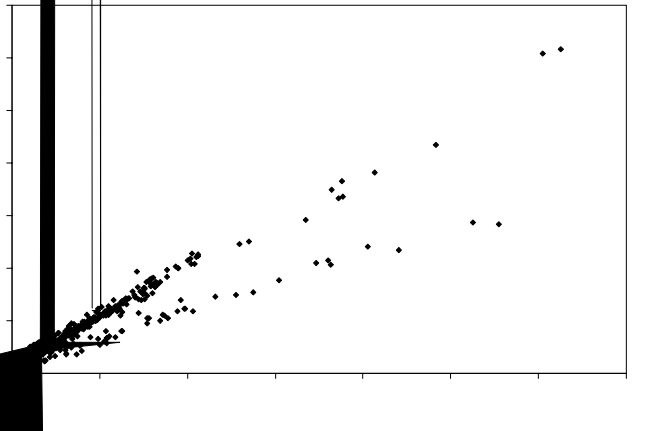

C2H2
y = 0.6557x
R2 = 0.5273
y = 0.4408x + 0.0002
R2 = 0.8682

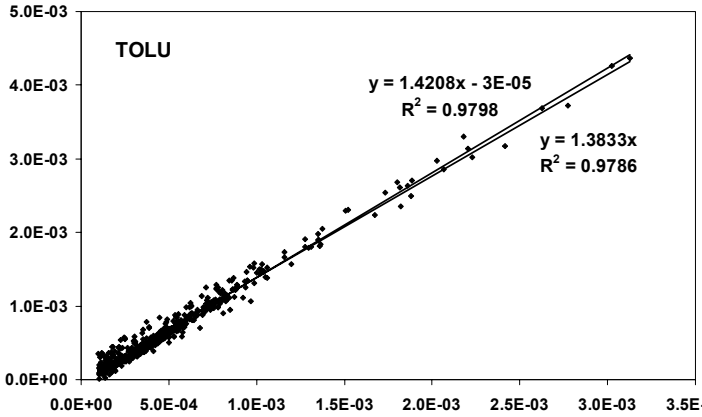

C2H6
y = 0.1366x
R2 = 0.3636
y = 0.0906x + 4E-05
R2 = 0.6332

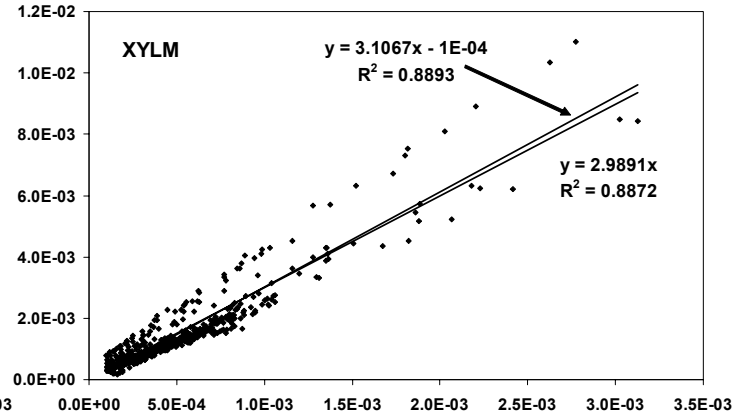

N_C4
y = 0.6142x
R2 = 0.5248
y = 0.4371x + 0.0001
R2 = 0.7197

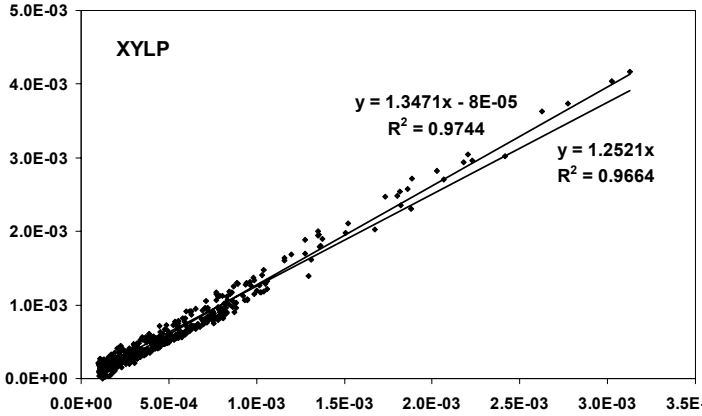

PRPE
y = 3.6581x
R2 = 0.934
y = 3.3638x + 0.0002
R2 = 0.9459

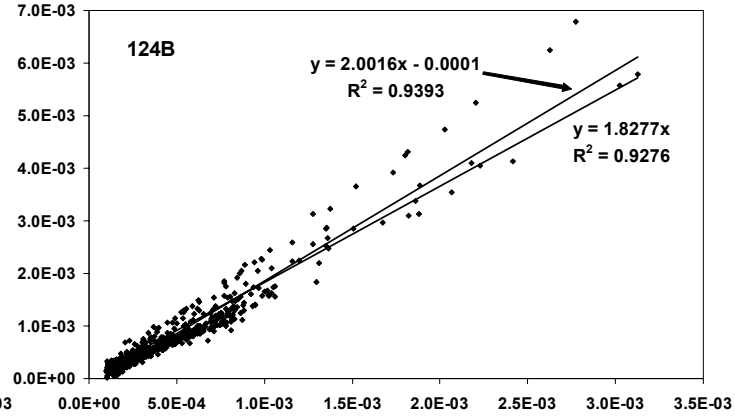

APNE
y = 1.0731x - 0.0002
R2 = 0.8989
y = 0.8049x
R2 = 0.8062

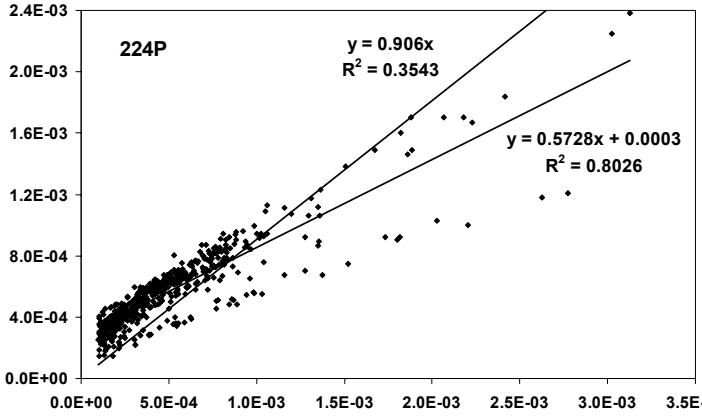


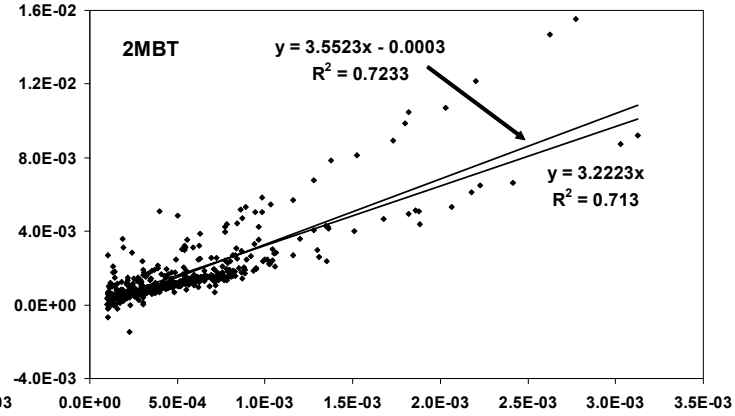

TOLU
y = 1.4208x - 3E-05
R2 = 0.9798
y = 1.3833x
R2 = 0.9786

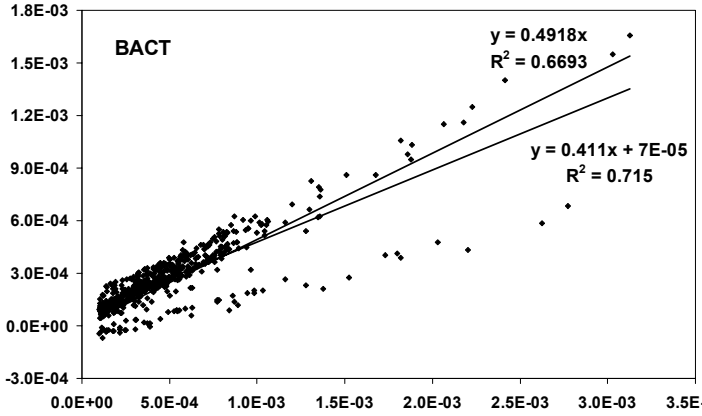

XYLM
y = 3.1067x - 1E-04
R2 = 0.8893
y = 2.9891x
R2 = 0.8872

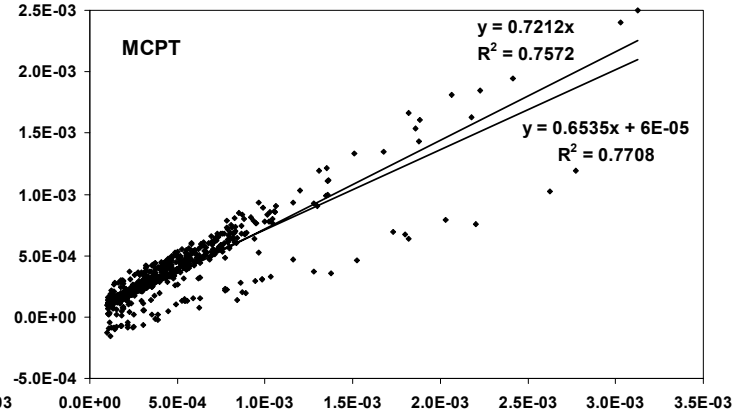

XYLP
y = 1.3471x - 8E-05
R2 = 0.9744
y = 1.2521x
R2 = 0.9664

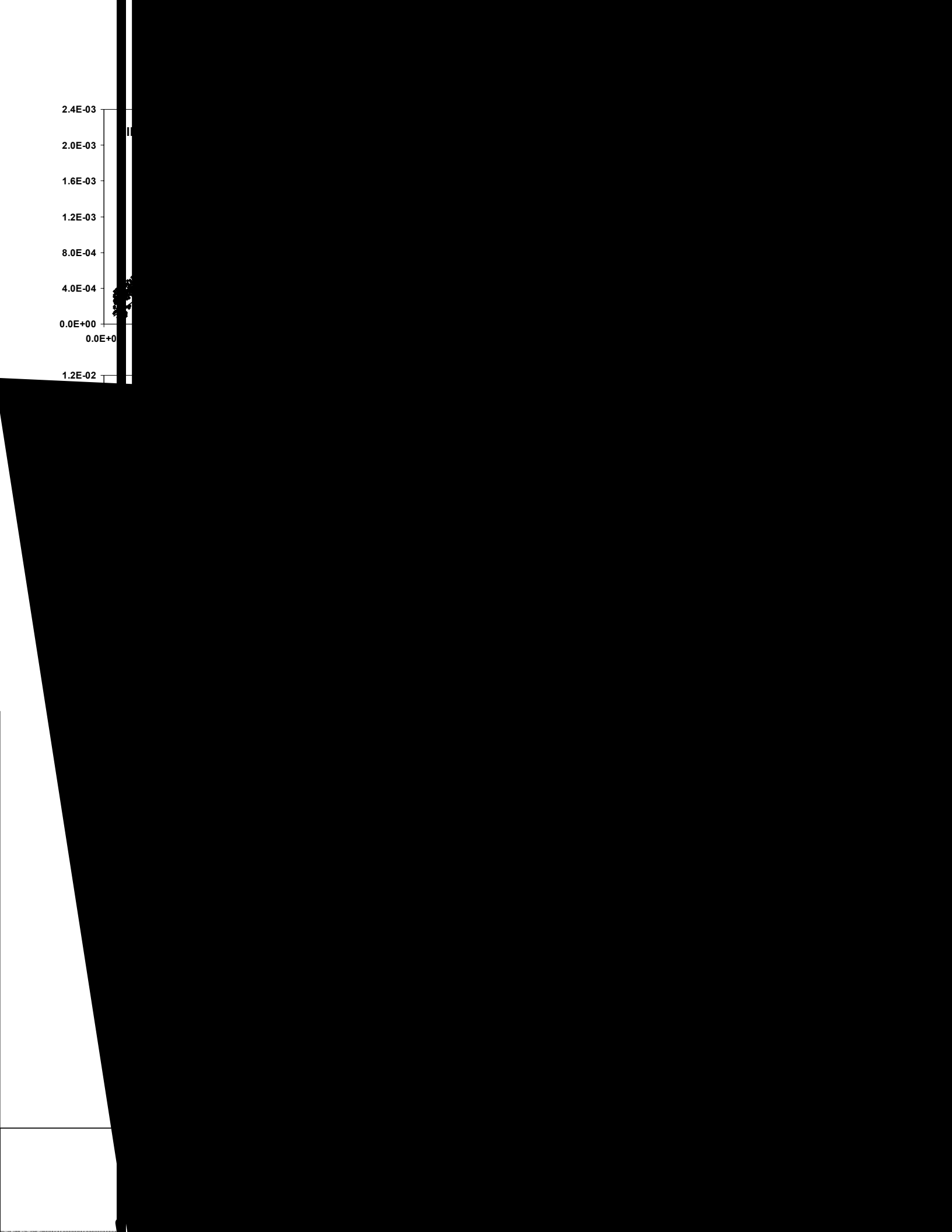

124B
y = 2.0016x - 0.0001
R2 = 0.9393
y = 1.8277x
R2 = 0.9276


224P
y = 0.906x
R2 = 0.3543
y = 0.5728x + 0.0003
R2 = 0.8026


2MBT
y = 3.5523x - 0.0003
R2 = 0.7233
y = 3.2223x
R2 = 0.713


BACT
y = 0.4918x
R2 = 0.6693
y = 0.411x + 7E-05
R2 = 0.715


MCPT
y = 0.7212x
R2 = 0.7572
y = 0.6535x + 6E-05
R2 = 0.7708


2.4E-03
2.0E-03
1.6E-03
1.2E-03
8.0E-04
4.0E-04
0.0E+00
0.0E+0
1.2E-02

Appendix C: List of reactions for organic species.

HCHO + HV = #2 HO2. + CO

HCHO + HV = H2 + CO

HCHO + HO. = HO2. + CO + H2O

HCHO + HO2. = HOCOO.

HCHO + NO3 = HNO3 + HO2. + CO

CCHO + HO. = CCO-O2. + H2O

CCHO + HV = CO + HO2. + C-O2.

CCHO + NO3 = HNO3 + CCO-O2.

RCHO + HO. = #.034 RO2-R. + #.001 RO2-N.
+ #.965 RCO-O2. + #.034 CO + #.034 CCHO +
#-0.003 XC

RCHO + HV = CCHO + RO2-R. + CO + HO2.

RCHO + NO3 = HNO3 + RCO-O2.

ACET + HO. = HCHO + CCO-O2. + R2O2.

ACET + HV = CCO-O2. + C-O2.

MEK + HO. = #.37 RO2-R. + #.042 RO2-N. +
#.616 R2O2. + #.492 CCO-O2. + #.096 RCO-O2.
+ #.115 HCHO + #.482 CCHO + #.37 RCHO + #.287 XC

MEK + HV + #.15 = CCO-O2. + CCHO + RO2-R.

MEOH + HO. = HCHO + HO2.

BALD + HO. = BZCO-O2.

BALD + HV + #.05 = #7 XC

BALD + NO3 = HNO3 + BZCO-O2.

CH4 + HO. = H2O + C-O2.

ETHE + HO. = RO2-R. + #1.61 HCHO + #.195 CCHO

ETHE + O3 = #.12 HO. + #.12 HO2. + #.5 CO +
#.13 CO2 + HCHO + #.37 HCOOH

ETHE + NO3 = RO2-R. + RCHO + #-1 XC + XN

ETHE + O3P = #.5 HO2. + #.2 RO2-R. + #.3 C-O2.
+ #.491 CO + #.191 HCHO + #.25 CCHO + #.009 GLY
+ #.5 XC

ISOP + HO. = #.907 RO2-R. + #.093 RO2-N. +
#.079 R2O2. + #.624 HCHO + #.23 METHACRO +
#.32 MVK + #.357 ISO-PROD + #-0.167 XC

ISOP + O3 = #.266 HO. + #.066 RO2-R. +
#.008 RO2-N. + #.126 R2O2. + #.192 MA-RCO3. +
#.275 CO + #.122 CO2 + #.592 HCHO + #.1 PROD2
+ #.39 METHACRO + #.16 MVK + #.204 HCOOH +
#.15 RCO-OH + #-0.259 XC

ISOP + NO3 = #.187 NO2 + #.749 RO2-R. +
#.064 RO2-N. + #.187 R2O2. + #.936 ISO-PROD +
#-0.064 XC + #.813 XN

ISOP + O3P = #.01 RO2-N. + #.24 R2O2. +
#.25 C-O2. + #.24 MA-RCO3. + #.24 HCHO +
#.75 PROD2 + #-1.01 XC

TRP1 + HO. = #.75 RO2-R. + #.25 RO2-N. +
#.5 R2O2. + #.276 HCHO + #.474 RCHO +
#.276 PROD2 + #5.146 XC

TRP1 + O3 = #.567 HO. + #.033 HO2. +
#.031 RO2-R. + #.18 RO2-N. + #.729 R2O2. +
#.123 CCO-O2. + #.201 RCO-O2. + #.157 CO +
#.037 CO2 + #.235 HCHO + #.205 RCHO + #.13 ACET
+ #.276 PROD2 + #.001 GLY + #.031 BACL +
#.103 HCOOH + #.189 RCO-OH + #4.183 XC

TRP1 + NO3 = #.474 NO2 + #.276 RO2-R. +
#.25 RO2-N. + #.75 R2O2. + #.474 RCHO +
#.276 RNO3 + #5.421 XC + #.25 XN

TRP1 + O3P = #.147 RCHO + #.853 PROD2 + #4.441 XC

ALK3 + HO. = #.695 RO2-R. + #.07 RO2-N. +
#.559 R2O2. + #.236 TBU-O. + #.026 HCHO +
#.445 CCHO + #.122 RCHO + #.024 ACET + #.332 MEK
+ #-0.05 XC

ALK4 + HO. = #.835 RO2-R. + #.143 RO2-N. +
#.936 R2O2. + #.011 C-O2. + #.011 CCO-O2. +
#.002 CO + #.024 HCHO + #.455 CCHO + #.244 RCHO
+ #.452 ACET + #.11 MEK + #.125 PROD2 + #-0.105 XC

ALK5 + HO. = #.653 RO2-R. + #.347 RO2-N. +
#.948 R2O2. + #.026 HCHO + #.099 CCHO +
#.204 RCHO + #.072 ACET + #.089 MEK +
#.417 PROD2 + #2.008 XC

ARO1 + HO. = #.224 HO2. + #.765 RO2-R. +
#.011 RO2-N. + #.055 PROD2 + #.118 GLY +
#.119 MGLY + #.017 PHEN + #.207 CRES +
#.059 BALD + #.491 DCB1 + #.108 DCB2 +
#.051 DCB3 + #1.288 XC

ARO2 + HO. = #.187 HO2. + #.804 RO2-R. +
#.009 RO2-N. + #.097 GLY + #.287 MGLY +
#.087 BACL + #.187 CRES + #.05 BALD + #.561 DCB1
+ #.099 DCB2 + #.093 DCB3 + #1.68 XC

OLE1 + HO. = #.91 RO2-R. + #.09 RO2-N. +
#.205 R2O2. + #.732 HCHO + #.294 CCHO +
#.497 RCHO + #.005 ACET + #.119 PROD2 + #.92 XC

OLE1 + O3 = #.155 HO. + #.056 HO2. +
#.022 RO2-R. + #.001 RO2-N. + #.076 C-O2. +
#.345 CO + #.086 CO2 + #.5 HCHO + #.154 CCHO +
#.363 RCHO + #.001 ACET + #.215 PROD2 +
#.185 HCOOH + #.05 CCO-OH + #.119 RCO-OH +
#.654 XC

OLE1 + NO3 = #.824 RO2-R. + #.176 RO2-N. +
#.488 R2O2. + #.009 CCHO + #.037 RCHO +
#.024 ACET + #.511 RNO3 + #.677 XC + #.489 XN

OLE1 + O3P = #.45 RCHO + #.437 MEK + #.113 PROD2
+ #1.224 XC

OLE2 + HO. = #.918 RO2-R. + #.082 RO2-N. +
#.001 R2O2. + #.244 HCHO + #.732 CCHO +

```
  #.511 RCHO + #.127 ACET + #.072 MEK + #.061 BALD
  + #.025 METHACRO + #.025 ISO-PROD + #-.054 XC

OLE2 + O3 = #.378 HO. + #.003 HO2. +
  #.033 RO2-R. + #.002 RO2-N. + #.137 R2O2. +
  #.197 C-O2. + #.137 CCO-O2. + #.006 RCO-O2. +
  #.265 CO + #.07 CO2 + #.269 HCHO + #.456 CCHO +
  #.305 RCHO + #.045 ACET + #.026 MEK +

  #.006 PROD2 + #.042 BALD + #.026 METHACRO +
  #.073 HCOOH + #.129 CCO-OH + #.303 RCO-OH +
  #.155 XC

OLE2 + NO3 = #.391 NO2 + #.442 RO2-R. +
  #.136 RO2-N. + #.711 R2O2. + #.03 C-O2. +
  #.079 HCHO + #.507 CCHO + #.151 RCHO +
  #.102 ACET + #.001 MEK + #.015 BALD + #.048 MVK
  + #.321 RNO3 + #.075 XC + #.288 XN

OLE2 + O3P = #.013 HO2. + #.012 RO2-R. +
  #.001 RO2-N. + #.012 CO + #.069 RCHO + #.659 MEK
  + #.259 PROD2 + #.012 METHACRO + #.537 XC

PRPE + HO. = #.984 RO2-R. + #.984 HCHO
  + #.984 CCHO + #.016 RO2-N. + #-.048 XC

PRPE + O3 = #.5 HCHO + #.5 CCHO + #.185 HCOOH
  + #.320 HO. + #.060 HO2. + #.510 CO
  + #.135 CO2 + #.260 C-O2.
  + #.17 CCO-OH + #.070 INERT + #.070 XC

PRPE + NO3 = #.949 RO2-R. + #.051 RO2-N.
  + #2.693 XC + XN

PRPE + O3P = #.45 RCHO + #.55 MEK
  + #-0.55 XC

BUTD + HO. = #.961 RO2-R. + #.039 RO2-N.
  + #.48 "HCHO + METHACRO + ISO-PROD"
  + #-1.039 XC

BUTD + O3 = #.06 "HO2. + HO."
  + #.25 CO + #.19 CO2 + #.5 " HCHO + METHACRO"
  + #.125 PROD2 + #.375 MVK + #.185 HCOOH
  + #-1.375 XC
```

```
BUTD + NO3 = #.920 RO2-R. + #.08 RO2-N.
  + #.92 MVK + #-.161 XC + XN

BUTD + O3P = #.25 HO2. + #.02 RO2-N.
  + #.23 "RO2-R. + CO + METHACRO"
  + #.75 PROD2+ #-1.77 XC

2MBT + HO. = #.935 RO2-R. + #.065 RO2-N.
  + #.935 CCHO + #.935 ACET + #-0.065 XC

2MBT + O3 =  #.7 R2O2. + #.156 C-O2.
  + #.7 CCO-O2. + #.856 HO. + #.156 CO
  + #.042 CO2 + #.7 HCHO + #.7 CCHO
  + #.3 ACET + #.102 CCO-OH
  + #.042 "INERT + XC"

2MBT + NO3 = #.935 "NO2 + R2O2. + CCHO + ACET"
  + #.065 "RO2-N. + XN" + #-.065 XC

2MBT + O3P = MEK + XC

C2H6 + HO. = RO2-R. + CCHO

C2H2 + HO. = #.1 RO2-R. + #.297 HO2.
  + #.393 CO + #.096 HCHO
  + #.607 GLY + #.297 HCOOH

C2H2 + O3 = #1.5 HO2. + #.5 HO.
  + #1.5 CO + #.5 CO2

C3H8 + HO. = #.965 RO2-R. + #.035 RO2-N.
  + #0.000 R2O2. + #.261 RCHO + #.704 ACET
  + #-.104 XC

N-C4 + HO. = #.079 RO2-N. + #.921 RO2-R.
  + #.413 R2O2. + #.632 CCHO
  + #.12 RCHO + #.485 MEK + #-0.038 XC

IPNT + HO. = #.095 RO2-N.
  + #.881 RO2-R. + #.902 R2O2. + #.780 CCHO
  + #.762 ACET + #.101 RCHO + #.038 MEK
  + #.094 XC + #.024 C-O2. + #.012 HCHO

N-C5 + HO. = #.145 RO2-N. + #.855 RO2-R.
  + #.650 R2O2. + #.147 CCHO
  + #.220 RCHO + #.238 MEK + #-.157 XC
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+ #.397 PROD2

224P + HO. = #.227 RO2-N. + #.403 RO2-R.
+ #.388 RCHO + #.133 MEK + #1.809 XC
+ #1.961 R2O2. + #.370 TBU-O. + #.717 HCHO
+ #.002 CCHO + #.380 ACET + #.027 PROD2

MCPT + HO. = #.306 RO2-N. + #.453 RO2-R.
+ #1.847 R2O2. + #.017 HCHO + #.689 RCHO
+ #.000 MEK + #.023 CO + #1.556 XC
+ #.239 CCO-O2. + #.003 RCO-O2. + #.003 PROD2

BACT + HO. = #.675 RO2-R. + #.120 RO2-N.
+ #.516 R2O2. + #.205 RCO-O2. + #.006 CO
+ #.116 CCHO + #.211 CCO-OH
+ #.172 RCHO + #.024 INERT
+ #.252 MEK + #.251 PROD2 + #.950 XC

C6H6 + HO. = #.236 PHEN + #.207 GLY
+ #.764 DCB1 + #.764 RO2-R. + #.236 HO2.
+ #1.114 XC

TOLU + HO. = #.085 BALD + #.234 CRES
+ #.116 GLY + #.135 MGLY + #.460 DCB1
+ #.758 RO2-R. + #.234 HO2. + #1.178 XC
+ #.156 DCB2 + #.057 DCB3
+ #.008 RO2-N.

XYLM + HO. = #.037 BALD + #.210 CRES
+ #.107 GLY + #.335 MGLY + #.347 DCB1
+ #.782 RO2-R. + #.210 HO2. + #1.628 XC
+ #.008 RO2-N. + #.290 DCB2
+ #.108 DCB3

XYLP + HO. = #.083 BALD + #.188 CRES
+ #.195 GLY + #.112 MGLY + #.709 DCB1
+ #.804 RO2-R. + #.188 HO2. + #2.432 XC
+ #.008 RO2-N. + #.012 DCB3

124B + HO. = #.044 BALD + #.186 CRES
+ #.364 MGLY + #.733 DCB1 + #.804 RO2-R.
+ #.186 HO2. + #2.730 XC + #.010 RO2-N.
+ #.063 GLY + #.079 BACL + #.027 DCB3

APIN + HO. = #.75 RO2-R. + #.25 RO2-N.
+ #.75 RCHO + #6.5 XC + #.5 R2O2.

APIN + O3 = #.081 RO2-R. + #.321 RO2-N.
  + #1.375 R2O2. + #.298 RCO-O2. + #.7 HO.
  + #.051 CO + #.339 HCHO + #.218 RCHO
  + #.345 ACET + #.002 GLY + #.081 BACL
  + #.3 RCO-OH + #3.875 XC

APIN + NO3 = #.75 "NO2 + R2O2. + RCHO"
  + #.25 RO2-N. + #6.25 XC + #.25 XN

APIN + O3P = PROD2 + #4 XC

MTBE + HO. = #.078 RO2-N. + #.743 RO2-R.
  + #.381 R2O2. + #.234 HCHO + #.719 MEK
  + #.939 XC + #.162 C-O2. + #.016 TBU-O.
  + #.024 ACET + #.007 PROD2 + #.155 INERT

ETOH + HO. = #.05 RO2-R. + #.95 HO2.
  + #.081 HCHO + #.960 CCHO

IPOH + HO. = #.953 HO2. + #.046 HCHO
  + #.046 CCHO + #.953 ACET + #.046 RO2-R.
  + #.001 RO2-N. +#-.003 XC

ACRO + HO. = #.25 RO2R + #.75 MARC
  + #.167 CO + #.083 HCHO + #.167 CCHO
  + #.083 GLY +#-.75 XC

ACRO + O3 = #.31 OH + #.81 HO2 + CO
  + #.315 CO2 + #.5 HCHO + #.5 GLY
  + #.185 HCOOH

ACRO + NO3 = #.031 RO2R + #.002 RO2N
  + #.967 MARC + #.031 CO + #.031 RCHO
  +#-1.003 XC

ACRO + O3P = RCHO

ACRO + HV = #.172 OH + #1.01 HO2
  + #.172 C_O2 + #.33 MARC + #1.182 CO
  + #.046 CO2 + #.34 HCHO + #.112 CCO-OH
  + #.046 INERT +#-.284 XC

DODC + HO. = #.542 RO2R + #.458 RO2N
  + #.768 R2O2 + #.011 RCHO + #.531 PRD2

Appendix D: Answers to RRWG Policy Questions.

1. What is the hypothesis that we want to test?
The hypothesis is whether or not reactivity scales that are calculated through three-dimensional regional air quality modeling, can offer a quantitative measure to rank different organic species, based on their relative importance in photochemical ozone production, and if such scale could prove useful and applicable in developing and evaluating VOC-based pollution control strategies.

2. What would be the affect on ambient air levels of substituting low reactive compounds for highly reactive ones?
The reduction in ozone concentrations due to such substitution shows high temporal and spatial variability. The effect of substitution is more in areas that are heavily affected by anthropogenic (NO_x and VOC) emissions, where high ozone concentrations are more of a concern. Since the 3D reactivities are calculated on a relative basis, a similar question is how big a substitution is required for each VOC to reach the same level of improvement in air quality.

3. Would controlling only the most reactive compounds (while exempting less reactive compounds) have any significant impact on ambient ozone levels?
While such large-scale substitution should have a significant effect on ozone levels, the specific reduction levels for each location and time, to some degree would depend on the original emission pattern for the domain and episode. It is also important to note that the calculated reactivity values (as well as the other defined reactivity scales) are incremental. Therefore, estimating the effect of large-scale substitutions would entail inaccuracies that stem from linearity assumption for reactivities.

4. How would low reactivity compounds emitted in large volume affect ambient ozone levels? Could widespread exemption of lower reactive compounds cause the ambient air quality standard to be violated in certain locations?
As mentioned before, extrapolating the results from incremental reactivities to large-scale substitution may not be very accurate. Such large change in emission characteristics can cause non-linear response in terms of reactivities. However, relative reactivities are fairly insensitive to such non-linearities. Evaluation of the effect of large volume of low reactivity compounds is beyond the objective of this project, but the findings suggest that if the increase in low reactivity VOC emissions is more or less coupled with respective decrease in the emissions of highly reactive compounds, the ozone levels will decrease in most places.

5. What is the geographical validity of reactivity scales? Are scales valid over the whole country or only in certain locations? If not, how large are variations? What would be the cause of the variations?
The scales that are developed as part of this project are relative scales. While absolute reactivities show a great deal of spatial variability, relative scales are fairly constant. These scales for different regions (remote NO_x-limited, or urban VOC-limited, or high biogenic areas), different episodes (with high or low ozone levels), different control

scenarios, and different domains (Western or Eastern US) are similar. The variability in the reactivity scales is mainly due to different emission pattern, chemical regimes, and meteorology.

6. How do initial conditions affect reactivity scales (i.e., VOC/NOx ratios)?
Our previous tests show that ozone sensitivity to initial ozone, NO_x, or VOC fades away fairly fast (2-3 days) into the simulation. As the first two days are considered ramp-up period, the effect of initial conditions is considered minimal. On the other hand, boundary conditions of NO_x/VOC may have a more significant effect on the absolute reactivity levels, but relative reactivity scales will remain fairly insensitive.

7. How does meteorology affect scales?
Meteorology is one of the major sources of variability in reactivity scales. Meteorology can affect the chemical dynamics of the atmosphere (temperature, sunlight, and humidity are all very important factors in ozone production), but more importantly it defines the emission distribution pattern (through transport) of the pollutants in the domain. For this reason, modeling different episodes and days is important. Relative reactivity scales for most species show low day-to-day variability, while some other species (e.g. formaldehyde) appear more sensitive to meteorological regime.

8. Do reactivity scales shift if reactivity is evaluated over different lengths of time? (i.e., would a scale evaluated over 8 hours differ from a scale evaluated over 5 days?)
We have evaluated different reactivity scales for 1 and 8-hour periods. For the most part, relative reactivity scales for those two averaging periods are very similar to each other.

9. What is sensitivity of scales to different conditions? For example, do compounds' position on the scale flip-flop with different conditions?
As mentioned before, reactivity values are sensitive to different environmental conditions. Domain-wide relative reactivity scales, on the other hand, are much less sensitive to factors like emissions pattern, meteorology, and chemical regime. Based on the results from different domains and episodes, the ranking of domain-wide relative reactivity scales is not greatly affected by those conditions.

10. Should we be looking at other kinds of scales than MIR scales? What other scales should we look at? Would we want to evaluate how other types of scales vary with varying conditions?
We have looked at three domain-wide relative reactivity scales, i.e. MIR-3D, MOIR-3D, and least square fit. Most of these scales are found to be very similar. Therefore, any **domain-wide** relative reactivity scale should result in a fairly similar ranking for VOCs. MOIR scale shows a high level of variability, and despite its regulatory importance, is not considered to be a robust scale.

11. What atmospheric model is used to evaluate validity of reactivity scales? Is this model one that is widely used and available to various independent researchers so that work can be verified and peer reviewed? Is a proprietary model of value if it is not widely accessible to everyone?

We used an updated version of Urban to Regional Model (URM), which has been used in a number of previous studies and is available to all interested parties. For a similar study we have used a different model (MAQSIP) for a different domain (California). The results of the two studies are very comparable.

12. What is the sensitivity of reactivity in the model? Are all compounds lumped into a few bins? Is carbon bond IV, which lumps compounds into 11 reactivity bins, sensitive enough to evaluate reactivity scales? Is there a better way of handling reactivity in models? If so, what?

We have calculated reactivity scales for about 32 explicit species, as well as 9 lumped VOCs, using SAPRC-99 chemical mechanism. A detailed chemical mechanism is favorable for reactivity study, and the results are more reliable.

13. Are effects of grams versus moles being considered? If a certain percentage of VOC is being reduced in a model, is this by weight or by number of moles? If one compound is being substituted for another in a computer run, is this substitution being made by weight or by number of moles? How will this affect the outcome of the experiment?

The incremental reactivities are calculated based on the unit mass (grams or moles) of VOC emitted. In the calculations, and because of the linear approximation of the reactivity, gram-based or mole-based perturbations give identical results. Of course, for each unit a different value for relative reactivity scales are calculated. The choice of the units, is mainly a regulatory decision.