6. APPLICATION OF THERMODYNAMIC EQUILIBRIUM MODEL (SCAPE2)

In this section, we update our previous analyses of which precursor species (ammonia or nitric acid) limit the formation of particulate nitrate in the SoCAB. The method of analysis consists of application of a thermodynamic equilibrium model (SCAPE2) (Kim et al, 1993a; 1993b; 1995; Meng et al, 1995a; 1995b) in conjunction with examination of the ambient measurements (Blanchard et al., 2000). Both methods require gas-phase measurements (ammonia and nitric acid) in addition to a variety of particulate species. Therefore, data from special studies are required; routinely collected data are insufficient. In previous work, we applied these methods to all data from the CADMP network and the 1987 SCAQS (see Section 2). Here, we analyze the measurements from the one-year PTEP study. The data were collected from March 1995 through February 1996 at five locations: Anaheim, downtown Los Angeles, Diamond Bar, Fontana, and Riverside-Rubidoux.

SCAPE2 predicted the partition between particulate ammonium and gas-phase ammonia, and between particulate nitrate and gas-phase nitric acid, within about 5 $\mu g\ m^{-3}$ for most of the samples (Figure 60). In many cases, the agreement between predicted and measured values was even closer. The model tended to underpredict the particulate ammonium concentrations and to overpredict the higher nitric acid concentrations (Figure 60). Given the resolution (24-hour) of the samples, and the temperature- and RH-dependent variations occurring between the gas and particle phases, better agreement between measurements and model predictions may be difficult to achieve. It is also possible that some samples were not particularly close to equilibrium (Wexler and Seinfeld, 1992), though samples that are thought to be furthest from equilibrium were excluded (Wexler and Seinfeld, 1992; Blanchard et al., 2000). The general level of agreement between measurements and predictions is adequate for application of the model.

Nearly all samples showed that particulate nitrate decreased in response to a 20 percent reduction of HNO_3; in many cases, the predicted decrease was close to twenty percent (Figure 60). In contrast, predicted particulate nitrate concentrations decreased by much smaller amounts in response to a twenty percent decrease in ammonia concentrations and decreases in sulfate concentrations left the particulate nitrate concentrations essentially unchanged. Thus, few samples showed any evidence of ammonia limitation. Emission changes that lower the rates of formation of HNO_3 are therefore predicted to lower particulate nitrate concentrations as well.

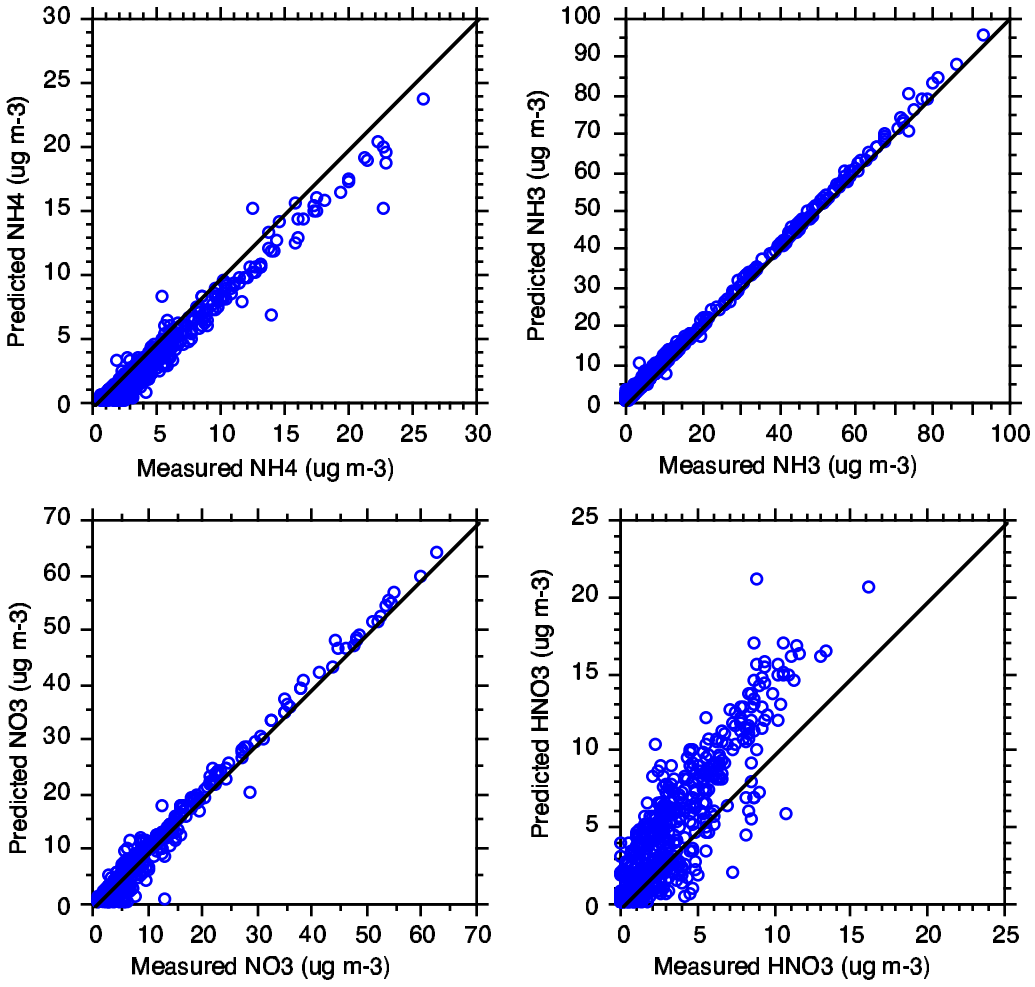

Figure 60. Predicted versus measured concentrations of ammonium, ammonia, nitrate, and nitric acid for 24-hour resolution data from the five sites of the PTEP study.

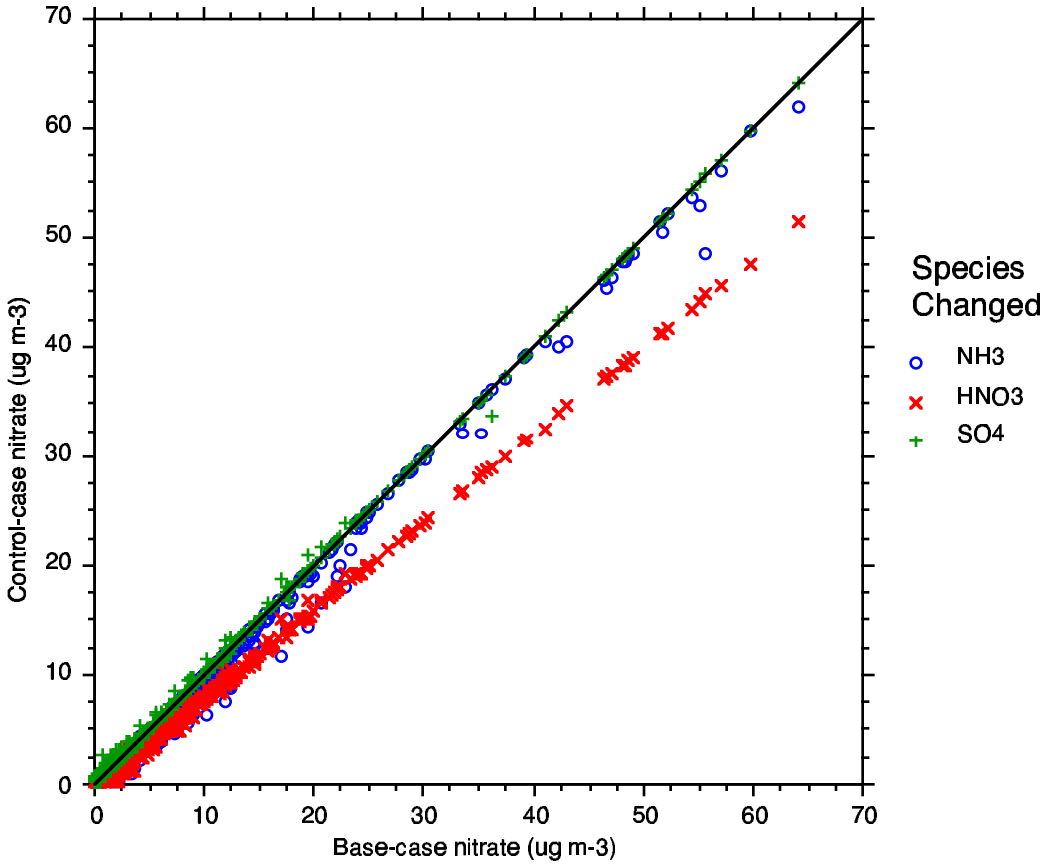

Figure 61. Control-case versus base-case nitrate concentration for 24-hour resolution data from the five sites of the PTEP study. The three control cases (species concentration reductions) were 20 percent decreases of total nitrate (HNO_3 plus particulate nitrate), total ammonia (NH_3 plus particulate ammonium), or sulfate.