Recent analyses of comprehensive ambient air pollution measurements in London have quantified the proportion of nitrogen oxides (NOX) in vehicle exhausts that is emitted as nitrogen dioxide (NO2). The analyses show that a greater proportion of NOX is emitted directly as NO2 than previously thought. For the 43 monitoring sites considered, the mean primary NO2 volume fraction was calculated to be 11.2%. Emissions of primary NO2 of this magnitude appear to explain approximately 21% of measured NO2 concentrations on average. However, at many congested locations with a high proportion of diesel vehicles, primary NO2 emissions are thought to explain over 30% of observed concentrations. For high percentile values of NO2, the primary NO2 contribution can dominate ambient concentrations. These results have implications for the management of air quality in urban areas since it is likely that directly emitted NO2 would respond differently to NOX control measures compared with that chemically produced in the atmosphere. In particular, the source apportionment of NO2 concentrations can be very different to NOX close to roads in London. The results also have implications for dispersion modelling studies of NO2, where it is generally assumed that a fixed 5.0% of the NOX emitted by vehicles is in the form of NO2. The implications of the increased use of particle traps on the London bus fleet that produce NO2 to assist in the oxidation of particles is also assessed.