

## Chemical mass balance

The management of **air quality** is a difficult but important problem. In general it involves identification of the sources of materials emitted into the air (*see* **Air quality indicators, pollutant specific**), quantitative estimation of the **emission** rates of the pollutants, understanding of the transport of the substances from the sources to downwind locations, and knowledge of the physical and chemical transformation processes that can occur during that transport (*see* **Atmospheric Dispersion: Chemistry**). All of those elements can then be put together into a mathematical model that is used to estimate the changes in observable airborne concentrations that might be expected to occur if various actions were taken. Such actions could include the initiation of new sources as new industries are built and begin to function, and the imposition of emission controls of existing facilities to reduce the pollutant concentrations.

However, the atmosphere is a very complex system (*see* **Meteorology**) and it is necessary to simplify greatly the descriptions of reality to produce a mathematical model capable of being calculated on even the largest and fastest computers. Thus, although significant improvements have been made over the past 20 years in the mathematical modeling of dispersion of pollutants in the atmosphere, there are still many instances when the models are insufficient to permit the full development of effective and efficient air quality management strategies. Thus, it is necessary to have other methods available to assist in the identification of sources and the apportionment of the observed pollutant concentrations to those sources (*see* **Source apportionment**). Such methods are called receptor-oriented or receptor models since they are focused on the behavior of the ambient environment at the point of impact (*see* **Concentration, ambient**), as opposed to the source-oriented dispersion models that focus on the transport, dilution and transformations that occur at the source and follow the pollutants to the sampling or receptor site.

The fundamental principle of receptor models is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne particulate matter in the atmosphere. This methodology has generally been referred to within the air pollution research community as **receptor modeling** [6, 7]. The approach to obtaining

a data set for receptor modeling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples. Alternatively, automated electron microscopy can be used to characterize the composition and shape of particles in a series of particle samples. In either case, a mass balance equation can be written to account for all  $m$  chemical species in the  $n$  samples as contributions from  $p$  independent sources:

$$x_{ij} = \sum_{k=1}^p c_{ik}s_{kj} \quad (1)$$

where  $x_{ij}$  is the  $i$ th elemental concentration measured in the  $j$ th sample,  $c_{ik}$  is the gravimetric concentration of the  $i$ th element in the material from the  $k$ th source, and  $s_{kj}$  is the airborne mass concentration of material from the  $k$ th source contributing to the  $j$ th sample.

There are a variety of ways to solve (1) depending on what information is available. If the number and nature of the sources in the region are known (i.e.  $p$  and  $a_{ik}$ ), then the only unknown is the mass contribution of each source to each sample,  $f_{kj}$ . This approach was first independently suggested in [9] and [19]. Miller et al. [9] modified (1) to explicitly include changes in composition of the source material while in transit to the receptor:

$$x_{ij} = \sum_{k=1}^p \alpha_{ik}c'_{ik}s_{kj} \quad (2)$$

where  $\alpha_{ik}$  is the coefficient of fractionation so that if  $c'_{ik}$  were the composition of the particles as emitted by the source,  $c_{ik}$  is the composition of the particles at the receptor site ( $c_{ik} = \alpha_{ik}c'_{ik}$ ). In practice, it is generally impossible to determine the  $\alpha_{ik}$  values and they are assumed to be unity ( $c_{ik} = c'_{ik}$ ). The collection of  $p$  source profile vectors forms a source profile matrix  $C$ .

Initially ordinary **least squares** was employed [5] for the estimation. Since different elements have quite different scales for their values (major elements at  $\mu\text{g m}^{-3}$  concentrations, minor elements at concentrations of hundreds of  $\text{ng m}^{-3}$  and trace elements at  $\text{ng m}^{-3}$  values), a weighted least squares regression analysis (*see* **Least squares, general**) has been used to fit six sources with eight elements for ten ambient samples [8]. In these analyses, the ambient elemental concentrations are weighted by the inverse

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of the square of the analytical uncertainty in that measurement.

It was recognized that there is uncertainty in the source profile values. The inclusion of this error is the statistical ‘error in  $x$ ’ problem that has been examined by a large number of investigators (*see Measurement error*). A mathematical formulation called effective variance weighting was independently suggested that included the uncertainty in the measurement of the source composition profiles as well as the uncertainties in the ambient concentrations [3, 16]. As part of this analysis, a method was also developed to permit the calculation of the uncertainties in the mass contributions. The effective variance weights are given by

$$(w_e)_{ii} = \frac{1}{\sigma_i^2 + \sum_{k=1}^p \sigma_{ik}^2 s_k^2} \quad (3)$$

where  $\sigma_i$  is the measured uncertainty in the ambient concentration  $x_i$  and  $\sigma_{ik}$  is the measured uncertainty for element  $i$  emitted by source  $k$ . Thus, the weights are dependent on the values of the regression coefficients, and an iterative algorithm is used to solve the problem. This approach has been described in [2] and [17]. This effective-variance least squares (EVLS) method has been incorporated into the standard personal computer software developed for the US **Environmental Protection Agency** (EPA) [18]. Because of the distribution of this EPA-approved model, it has become virtually mandatory to use EVLS in receptor modeling for regulatory purposes. It has thus been widely applied and those results are summarized in [12].

Because of limitations of performing the least-squares analysis, it is useful to have additional techniques that can help to determine the applicability of source profiles to the particulate apportionment problem being solved. These methods have been developed as solutions to the problem of calibrating multivariate chemical analysis instruments (*see Calibration*), but these methods can be applied to the receptor modeling problem. The methods applied to date include partial least squares [4, 13–15], **simulated annealing** [10], **genetic algorithms** [1] and backpropagation artificial **neural networks** [11]. In particular, the artificial neural network showed better results with respect to **collinearity** of sources. However, these methods have not been extensively tested in solving actual chemical mass balance problems.

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(See also **Chemometrics; Atmospheric Dispersion; Heavy gases; Emission inventory; Turbulent diffusion**)

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