AIChE

Atmospheric and Hydrological Transport Modelling of SOx Emissions in a Unique Verification Context

B. C. McLellan
Centre for Social Responsibility in Mining, Sustainable Minerals Institute, The University of Queensland, Brisbane, QLD 4072, Australia

A. Dicks
Sustainable Energy Research Group, School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

J. C. Diniz da Costa
Division of Chemical Engineering, School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

DOI 10.1002/aic.11985
Published online August 24, 2009 in Wiley InterScience (www.interscience.wiley.com).

In this work, we developed a conceptual model incorporating atmospheric transport and hydrological removal of sulfur compounds from a single isolated source. A process engineering approach with conceptual tanks, reactors, pipes, and valves is used for environmental transport modeling. The work includes verification of the model using current data and historical soil sulfur data from a study 23 yrs earlier, collected from sites in a forest and within 20 km from an isolated coal-fired power plant. This verification opportunity is unique in that the power plant is the single major pollutant source within the airshed. In the conceptual process engineering model, environmental relationships with local soil conditions and climate are modeled. The model is validated for three sampling sites, and a sensitivity analysis shows that rainfall has the greatest variance among several other parameters, including sulfur emissions, dry deposition rate, runoff factor, permeability factor, and airshed dimensions. The model is shown to be suitable for a location-specific sustainability metrics application, but it has limitations that further research could improve on including the incorporation of more complexity with the modeling of ground and surface water flows, atmospheric and soil reactions, and vegetation effects. © 2009 American Institute of Chemical Engineers, *AIChE J,* 56: 815–824, 2010

Keywords: Australia, sulfur, acidification, transport, model

Introduction

Emissions transport is one of the key components of predicting the actual impact of a process or plant on its local environment. Furthermore, the fate and effect of those emissions are based primarily on their transport, absorption and

Correspondence concerning this article should be addressed to B. C. McLellan at b.mclellan@uq.edu.au

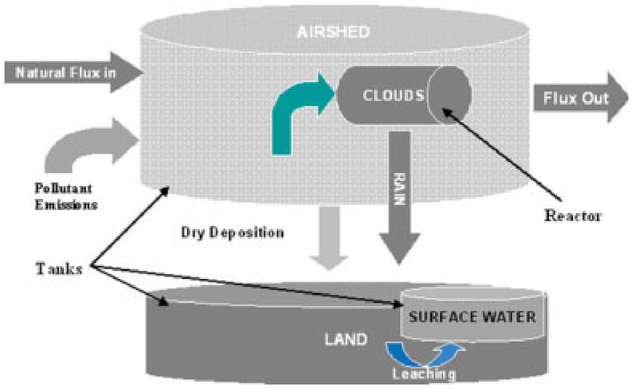

Figure 1. Process modelling of environmental transport and reaction in a sub-airshed.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

reaction within the air, soil and vegetation of that location. Hence, measurement and prediction of sustainability of a process in a given location relies on knowledge of the coupled hydrological-atmospheric transport and reaction of the emissions. Existing models of contaminant transport are numerous, but they tend to work only within a specific medium—i.e., groundwater, water, or air. The complexity of each individual modeling task leads to this natural division, but discrete models of the environmental transport of emissions, if not linked together, cannot provide a full picture of the environmental interactions of industrial operations. The emissions-transport model (ETM) described in this work was developed to be incorporated into a location-specific sustainability model, but it offers some interesting insights even in isolation from the broader model.

In any environment, there are natural processes occurring at any time in tandem with direct and synergistic impacts deriving from human activities. The intention of sustainability assessment or any general environmental impact assessment is to separate the natural from the anthropogenic emissions and subsequent effects. It is difficult to verify the contribution of individual point sources to contaminant levels in most parts of the developed world, where it is rare to encounter a single-point source contributor in any given airshed. In many industrialized nations, the complexity of this exercise is enormous, because in any environment of concern, there is a large matrix of emissions from a multitude of industries.[1–4] Australia is in the ideal situation for the verification of contaminant transport models because of the availability of airsheds with single point source contributors, such as coal-fired power stations.[5] The current work aimed to simulate sulfur deposition and hydrological transport, with verification using historical data from one such isolated emitter. Of the emissions from the plant, sulfur* was selected for the purpose of model validation as one of the few contaminants, which was monitored intermittently over a period of 23 yrs. In addition, sulfur has some comparative models for other countries[6] and one of the most significant in terms of potential impacts.[7,8]

*Sulfur compounds are assumed to be largely in the form of sulfur oxides (SOx) formed during combustion, of which SO_2 is assumed to be the key component. The model is developed based on parameter values for SO_2.

To create a model that could facilitate the integration of location-specific factors into a sustainability assessment, the desire was to reduce the complexity and data requirements as much as possible. For this particular application, relative ease of applicability (within acceptable limits of error) was viewed as the highest priority, rather than ''pinpoint'' accuracy. Hence, the model was developed from first principles, based on a process engineering approach, and by using easy-access data as far as possible. Material flows and some atmospheric reactions were included in the model. Physical parameters and climatic conditions for the specific region in question—in particular, the rainfall and wind patterns and local soil permeability factors—were key elements in the behavior of emissions transport. Short-term dynamic processes, which can affect the accuracy of the model, such as extreme variation in highly localized rainfall, vegetation species, weathering rate, deposition of acid-neutralising compounds, decomposition rate of litter, and soil matter,[9–11] are difficult to incorporate in the model without an intricate knowledge of the particular sites and their monitoring that is beyond the resources or practical limitations of any organization.[10] These processes were, therefore, not included; however, the results of the model are shown to be within reasonable bounds of error, even given these omissions.

Emissions Transport Model

Conceptual approach

The process model for emissions transport (the ETM) based on a series of ''tanks'' was shown to be sufficient for the purpose of demonstration in the context of a new sustainability metrics model,[12] although the accuracy may be improved using more complex models.[13,14] Airsheds and soil are modeled using a set of simple ''fixed-box'' model tanks connected in series radially outward from a central emissions point, with reactions assumed to occur in reactors within the tanks (Figure 1). A number of sub-airsheds are linked together to model the overall transport of emissions throughout an airshed (Figure 2).

As shown in Figure 1, the pollutant is emitted to the first sub-airshed, where it is assumed to be instantaneously diluted to give a uniform concentration across the sub-airshed. Based on a percentage of cloud cover, some of the pollutant enters clouds within the airshed, where most atmospheric aqueous-phase reactions occur. Pollutant is deposited to soil and water via both dry and wet deposition, whereas some of the remaining airborne pollutant is passed on to the next sub-airshed in a wind-related flux. Some of the deposited pollutant is leached from the soil to the water-bodies within the sub-airshed.

As theoretical mixing volumes, rather than actual tanks, the sub-airsheds can be modeled as volumes of any geometrical shape. Here, the model has been considered in terms of cylindrical tanks, which lend themselves to ease of calculation as separate sub-airsheds, but not necessarily when they are placed as a part of the complete model. Emissions are assumed to travel only in a radial direction from the plant, carried by the wind (Figure 3). Using this assumption, the wind rose data from the Australian Bureau of Meteorology is the key data used for dispersion modeling. Intuitively,

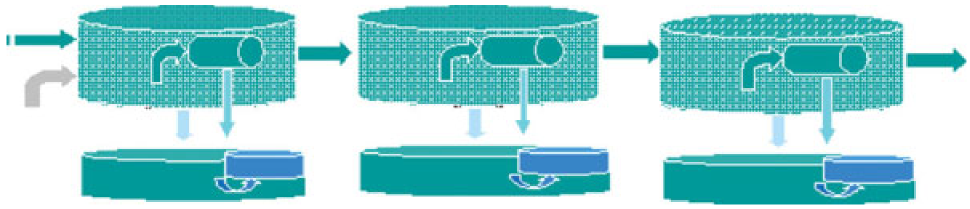

Figure 2. Linked sub-airsheds for overall airshed modelling.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dilution of emissions occurs with increasing distance, hence, the sub-airsheds in the model increase in volume with increasing distance from the plant.

Existing dispersion models typically use Gaussian plume models for the transport of air-borne emissions, but few of them apply this any further than determining the concentrations and deposition rates at various distances from the source. The current methodology allows variations in local conditions to be fitted by adjustment of environmental parameters (such as soil permeability) within the airshed or indeed any individual sub-airshed. By decreasing the radii of the tanks and, therefore, increasing the number of tanks in the same area of coverage, a finer-grained discretion may be achieved; however, the greater the number of tanks, the higher the data requirements.

Expanding the process engineering approach further, we can develop a process flow diagram for the environment-process system (Figure 4). The distribution of contaminant between clouds and the remaining "clear air" is modeled as a flow splitter, whilst the environmental relationship between rainfall and leaching is modeled as a flow control loop.

Ground water and surface water reservoirs have not been modeled here due to the lack of historical data on the relevant contaminant concentrations, but they are considered to be the ultimate environmental sink for contaminants. It is recommended that further work should examine the integration of ground and surface water quality into the model, with monitoring data collected for validation purposes.

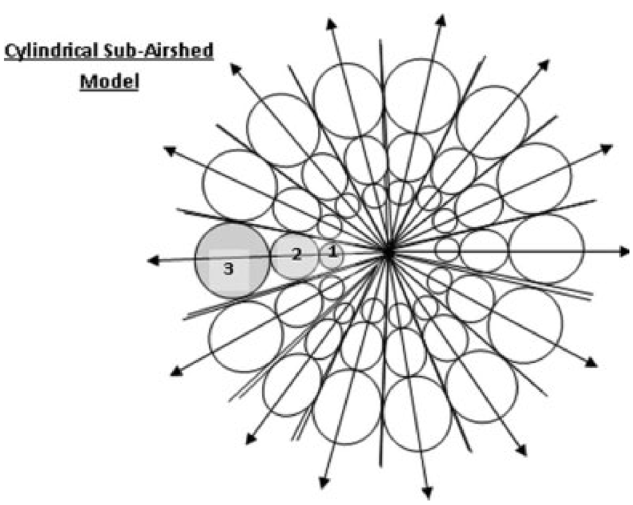

Figure 3. Multiple "sub-airsheds" with radial direction of emissions flow as utilised in the ETM.

Monitoring data from a number of sites around an existing power station, compared for recent and historical data, gave the "flow control" relationship between soil permeability, runoff rate, and the annual rainfall, such that the deposited, retained, and leached sulfur could be determined. Table 1 shows the characteristics of the three sites examined.

Equations resulting from the process approach

Following the process approach, a mass balance over the relevant tanks and application of first principles was used to determine change in concentration over time.

Temporal Variation of Contaminant Concentration in Sub-Airsheds. Initially, a dynamic modeling approach was taken. Using the innermost sub-airshed as an example, a simple mass balance of the form:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

we derive the following equation:

$$\frac{dM}{dt} = NF_{\mathrm{i}} + E_{\mathrm{i}} - NF_{\mathrm{o}} - D \tag{1}$$

However, it was shown that the equation rapidly approaches steady state under the conditions of atmospheric transport. Under the assumption of steady state, (for the example of the innermost airshed tank, tank 0†) this leads to the concentration equation as follows:

$$c = \frac{b.v.SA_1 + E_{\mathrm{i}}}{v.SA_2 + u.FSA} \tag{2}$$

Clouds. Clouds can be incorporated in the model, either as reactors or merely as vessels, to allow a different route for deposition—i.e., wet deposition. Cloud contaminant concentrations may be assumed to be in equilibrium with the surrounding atmosphere, with concentrations determined by Henry's law (Eq. 3).

$$c_{\mathrm{r}} = k'.\left(\frac{c_{\mathrm{i}}}{64.n_{\mathrm{air}}}\right) \tag{3}$$

where:

k = Henry's law constant[15]

n_{air} = number of micromoles of air in 1 $m^3 \approx 44.6 \times 106$ (at 273 K and 1 atm)

†Tanks are numbered starting at the centre (Tank 0) and moving radially outward, with further subscripts used to denote the direction (e.g., NE for North-East)

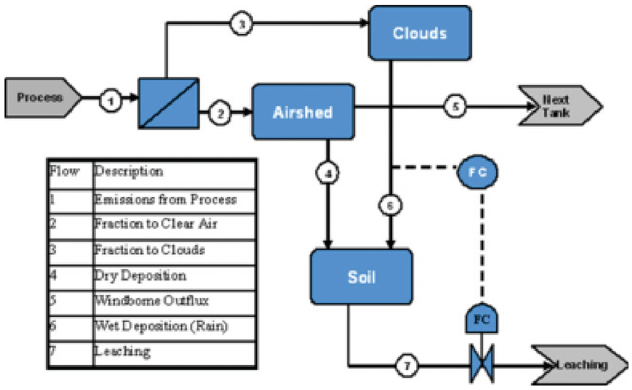

Figure 4. "Single tank" process flow diagram for the ETM tank.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$c_i/64$ = Molar concentration of sulfur (as sulfur dioxide) in air in tank "i" (μgmol/m^3)

c_r = Concentration of sulfur in rain water (μg/m^3).

For the moment, we assume the form of the contaminant is unimportant, so that we can disregard aqueous reactions. Thus, incorporating the rate of rainfall, the cloud mass balance becomes Eq. 4, as follows:

$$0 = q_r.k.\frac{c_i}{64.n_{air}} - q_r.c_r \tag{4}$$

where:

q_r = Volumetric rainfall (m^3/s)

Because the air tank concentration is assumed to be in steady state, the concentration of contaminant in the air in each sub-airshed and, hence, the concentration of contaminant in rain water is constant within each tank.

Temporal Variation of Contaminant Concentration in Soil. The soil tank is of much interest due to the potential for deposition resulting in impacts, such as soil acidification and land contamination, which could cause health impacts on flora and fauna. The inputs and outputs to the soil are indicated in Figure 5.

Thus the mass balance over the soil may be written as follows:

$$\frac{dM}{dt} = u.c_1.FSA.(1-\mu) + q_r.c_r.FSA.(1-\mu) - r_p.FSA.(1-\mu) - K_L q_r c_s - r_s \tag{5}$$

K_L here is a factor incorporating the fraction of rainfall that is removed by runoff $(F)^{\ddagger}$. K_L is also the control function of the flow controller in Figure 4. The value of F is related to the rate of runoff (slow, medium, or high, as classified in the original soil study).

$$K_L = F\left(\frac{q_{r(t)}}{q_{r(N)}}\right) \tag{6}$$

‡It must be noted that in the original mass balance, K_L was taken to represent all sulfur removed by rainfall. In subsequent analysis, it became apparent that the runoff factor was the strongest contributor to this term and that a second control factor for permeability should be incorporated in the model as K_P, which has the additional benefit of allowing closer fitting to the data.

Table 1. Examined Site Details Relevant to the Model

Site Characteristics	Site 15	Site 17	Site 32
Landform	Hillslope (3°)	Hillslope (6°)	Footslope (3°)
Drainage	Imperfect	Well drained	Poor
Permeability	Moderate	High	Slow
Permeability factor G	140	70	2500
Runoff rate	Moderately rapid	Very slow	Moderately rapid
Runoff factor F	2.2	1.4	2
Distance from stack (km)	19.3	7	4.3
Elevation (m)	550	590	400
Wind direction probability (%)	20.0	9.3	23.9
Atmospheric SO_x concentration (μg/m^3)	3.09	2.94	13.21

With an initial assumption of a dynamic model, the general solution of the differential equation can be derived, assuming no soil reactions or removal by vegetation, the mass balance may be solved to give:

$$c_s = \frac{(u.c_1 + q_r.c_r)}{K_L.q_r} - \alpha.e^{\frac{K_L.q_r FSA.(1-\mu)}{V_s}t} + K_P \tag{7}$$

where the factor α can be determined from the initial conditions: $t = 0$, $c_s = c_{s0}$.

The constant of integration (K_P) is defined to incorporate a factor (G), based on the permeability of the soil, which determines the relative effect of permeating rainwater on the bulk neutral soil component concentration (c_{s0}).

$$K_P = G\left(\frac{q_{r(N)}}{q_{r(t)}}\right)c_{s0} \tag{8}$$

K_P effectively acts as a flow controller on the outlet stream of the tank, determining how rapidly the bulk soil sulfur concentration will decrease through permeation, and adds a further control function to the model, which allows better fitting to the data. K_L largely determines how much deposited sulfur is washed out of the soil with runoff and

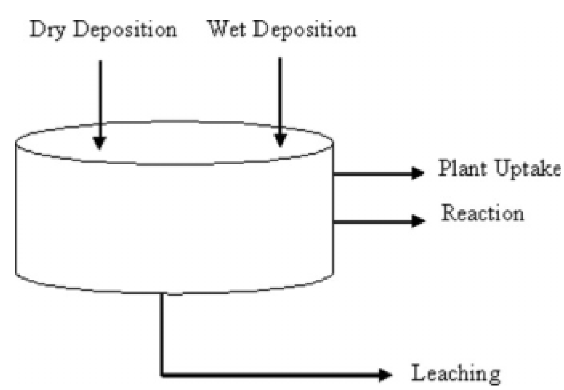

Figure 5. Inputs and outputs to the soil "tank."

Table 2. Model Parameters

Parameter	Symbol	Model Value	Reference
Background atmospheric SO_x concentration ($\mu g/m^3$)	b	1	Gilmour et al.[21]
Dry deposition rate (m/s)	u	0.005	Seinfeld and Pandis[15]; Gilmour et al.[21]
Henry's law constant (SO_x)	k	1.23	Seinfeld and Pandis[15]
Emissions (SO_x) (t/yr)	E_i	27,000	
Wind speed (m/s)	v	Direction-specific	Tarong[20]
Rainfall (mm/yr)	q_r, q_N	Year-specific	Nanango[20]
Runoff factor	G	70 (slow)–2500 (fast)	Site dependent; correlation with Plenderleith[22] (see Table 3)
Permeability factor	F	1.4 (low)–2.2 (high)	Site dependent; correlation with Plenderleith[22] (see Table 3)
Height of airshed "tanks" (km)	h	1.1	–
Soil depth (m)		0.1	as per monitoring[22]
Surface water depth (m)		1	–
Surface water coverage (%)	μ	1–5	estimated from maps[23]
Tank 1 radius (km)	r	1.5	–

how much remains on the surface to infiltrate into the soil. In this way, K_L acts as a flow splitter on the inlet streams to the tank.

The location-specific factors K_L and K_P are used to adjust the fraction of rain over a neutral, average value that contributes to washout of contaminants. This neutral value (qr(N)) is the annual historical average rainfall. Each site has its own permeability and runoff rates, which show a close correlation to the contaminant concentrations. The relevant site details for deriving key parameters G and F are given in Table 1.

The dynamic component of the solution will quickly approach zero as time increases, hence, steady state will quickly be reached. Steady state is a typical assumption in acid deposition and critical load work.[16–18] In the current instance, the natural system being examined is a forest with minimal anthropogenic interaction. Because this work investigates the environmental effects over a 23-yr period, any short-term dynamic effects are considered to be insignificant. Therefore, for the purpose of this work, these biological parameters are assumed not to be limiting factors on the concentration of sulfur in the soil, in accordance with the findings of Quilchano et al.[19] The concentration of sulfur in soil was assumed to be the same as the water in contact with the soil. The steady state solution to the mass balance would, therefore, become as follows:

$$c_s = \frac{(u.c_1 + q_r.c_r)}{K_L.q_r} + K_P \qquad (9)$$

This can be modeled in a spreadsheet by discretisation into yearly values, which allows the incorporation of annual rainfall data (obtained from the Australian Bureau of Meteorology[20]). The rainfall and wind data is readily available,[20] whilst the initial model values of remaining parameters are given in Table 2.

Results

ETM simulation

To verify and fit the model with historical data, three sites were selected for examination. In the original study, greater than 30 sites were examined,[22] however, not all of these were found to be appropriate for the purposes of this model, because many were located on or adjacent to agricultural land, which may have been influenced by other sulfur sources than the power station. The three selected sites were in forest zones around the plant. Data from the original study[22] and from a recent repeat measurement were used to fit and examine the performance of the model as described below.

The following graphs show the soil concentration variation over time given by the model, with a calculated baseline value (indicating the soil concentration as it would be without the plant), and historical data with error bars based on the variation of sample measurements for each year (as obtained from the original study). The variability of sample measurements is largely attributable to the fact that five samples were taken across a 20 m × 20 m sample site, where specific leaf deposition, runoff characteristics, and soil properties could affect the sulfur content. Variability of results due to error in analytical techniques was shown to have a lesser effect than inherent soil variability. The calculated baseline is solely based on background sulfur values (i.e., with no power plant in the airshed). For comparison purposes, the model can provide information on how the sulfur concentration of the soil varies in the case of: (i) baseline for background concentration only, (ii) full loading as conventionally used showing continuous accumulation of sulfur

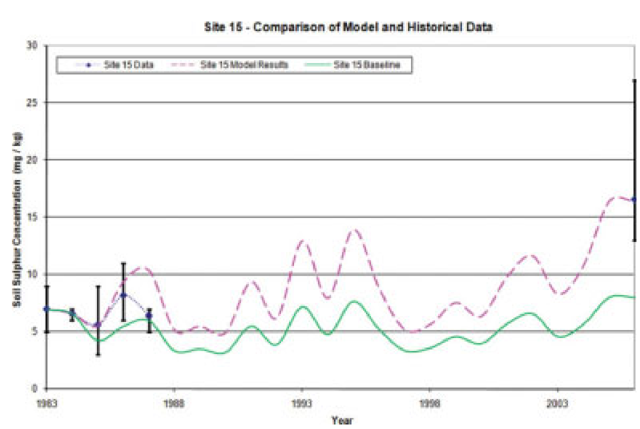

Figure 6. Site 15—soil concentration performance—model, baseline, and historical data.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

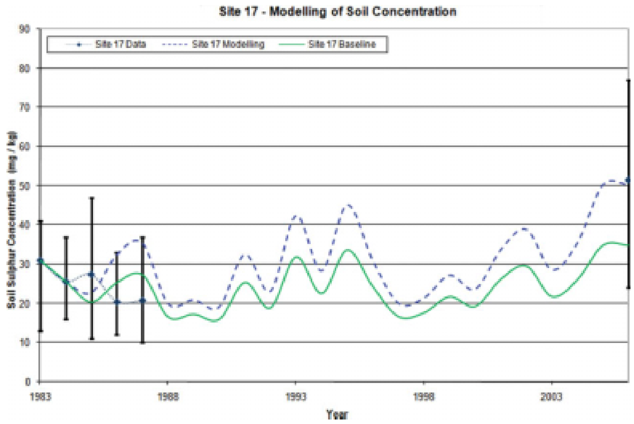

Figure 7. Site 17—soil concentration performance—model, baseline and historical data.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

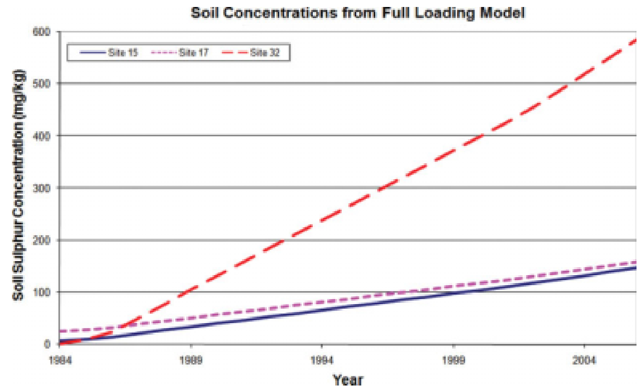

Figure 9. Full-loading model behaviour on soil sulfur concentration.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

on soils, and (iii) the model based on plant emissions incorporating environmental interaction. Calculated baseline is indicated in the legend as "base," simulation results as "model," and historical data is indicated by the site number.

It is seen from Figure 6 to Figure 8 that the performance of each site is very similar, with soil characteristics and atmospheric transport accentuating or decreasing the effect of variations in rainfall. It is also noted that the soil sulfur concentration increases toward the end of the period. This is due to the drought conditions that have prevailed over recent years in the area, which have led to reduced removal by leaching and runoff.

Variance between samples across a single site (as indicated by error bars on the graphs) can be quite wide because of localized differences in soil sulfur distribution. This may be due to the processes not included in the current model and is a consequence of examining complex real world phenomena. One method suggested to overcome this was to create a narrower sample site, but this would also require more numerous monitoring sites to improve overall reliability of the model.

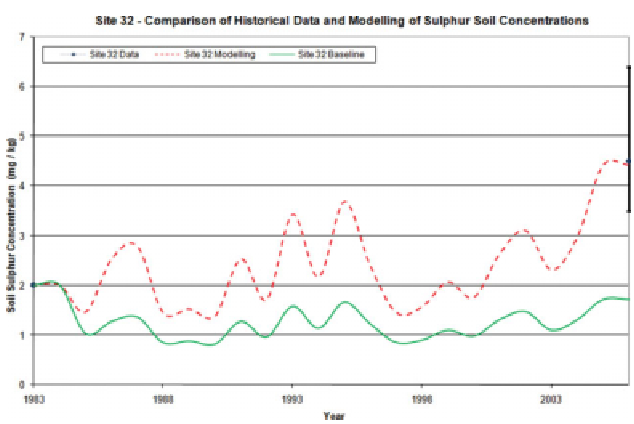

Figure 8. Site 32—soil concentration performance—model, baseline and historical data.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In comparison with the model presented, the situation, given no environmental processes other than dry deposition (the logical conclusion of isolated atmospheric transport models), would lead to the situation shown in Figure 9. However, the measured sulfur content is significantly lower than would be predicted in this "full-loading" situation, which indicates that the current model, which fits the observed data well, is more realistic—that in fact much of the deposited sulfur is removed by environmental processes. This has direct consequences for existing sustainability models, because it indicates that a loading-only model is not applicable to all situations, as actual environmental processes can reduce the overall impact of an emission.

Sensitivity analysis

In the development of the ETM model, all the parameters were assessed in a thorough sensitivity analysis to determine the key factors affecting model performance and to ensure alignment with theoretical underpinnings and robust modeling of the environmental effects of emissions. The effect of varying the parameters of the ETM on the subsequent response of the model is analyzed in Table 3. Each of the key parameters shown was increased and decreased by 20% (one parameter at a time), the model response in soil sulfur concentration observed, and the average percentage change from the accepted values recorded. The parameters that impacted most on the model performance were the yearly rainfall, average rainfall, runoff factor, and dry deposition velocity.

The yearly rainfall produced the largest deviation from the standard model, with a variation of 20% that causes a variation of between 26 and 47% at Site 15. This has many implications—both for the model and for the local impact of Australian emissions sources in general.

In terms of the model, error may enter into the assessment of each individual site if the annual rainfall is not relatively constant across all tanks or if there is an extreme variation within a single tank. This may be one source of error causing the model to deviate from the historical data at times. In terms of the local impact of Australian emissions sources,

Table 3. Percentage Variation in Soil Sulfur Concentration from the Base Model in Response to 20% Parameter Variation

	Percentage Change in Sulfur Concentration in Response to Parameter Variation of 20%					
Parameter	Site 15 (−20%)	Site 17 (−20%)	Site 32 (−20%)	Site 15 (+20%)	Site 17 (+20%)	Site 32 (+20%)
Neutral rainfall	−20	−20	−20	+20	+20	+20
Process emissions	−9.36	−6.9	−8.37	+9.36	+6.9	+8.37
Dry deposition rate	−14.09	−10.77	−9.45	+13.99	+10.73	+9.43
Yearly rainfall	+47.32	+41.93	+39.80	−26.59	−24.19	−23.24
Runoff factor (F)	+17.86	+13.55	+11.84	−11.91	−9.03	−7.89
Permeability factor (G)	+7.14	+11.45	+12.57	−4.76	−7.63	−8.38

with the current national drought and potential under a climate change paradigm to have reduced annual rainfall, the soil sulfur concentration (and, hence, the potential for soil acidification) may increase rapidly. This could be cause for concern and is something that Australian decision makers should keep in mind. Likewise, the average annual rainfall has shown a decrease over the past 30 years.[20] If this trend continues, then the sulfur levels in the soil could be raised to a new steady state. If the average rainfall and sulfur levels do not return to their previous levels, then the model would need to be reset around the new averages.

The effects of runoff factor and dry deposition rate are of lesser concern, given that the model remains within the bounds of error under the variation of these factors. The runoff factor is site specific, which can lead to difficulty in prediction of environmental response if the factor deviates too far from the best fit, however, given a simple classification of any site, such as that used in the original study, the model can be fitted with reasonable confidence.

From the sensitivity analysis, the model may be considered to be appropriately responsive to variations in parameters, but robust in regards to the behavior compared with historical data.

Comparison of the ETM with existing models

To confirm the validity of the ETM, it was compared with two existing models—the AUSPLUME Gaussian plume software and the RAINS-ASIA acid deposition software.[6] From these comparisons, it was hoped to ascertain the level to which the simplified model could be trusted in comparison with more complex models. The parameters of interest were the deposition and atmospheric concentration of SOx.

Comparison with AUSPLUME. AUSPLUME is an Australian-based Gaussian plume model, developed by Monash University and the Victorian Environmental Protection Agency.[24] A terrain file and meteorological file were developed using geographic and meteorological data and used in AUSPLUME for comparison with the current model.

From Figure 10, it is apparent that the current model provides concentrations that are close to those provided by the AUSPLUME software. Although it has been surpassed for specific air pollutant transport and reaction by The Air Pollution Model,[25] the AUSPLUME model is widely used in the Australian context to model atmospheric emissions transport[21,26] and is typical of a Gaussian plume model. With the close correlation shown with AUSPLUME results, the model can be used with reasonable confidence to predict the atmospheric concentration.

Comparison with RAINS-ASIA. RAINS-ASIA (Regional Air Pollution Information and Simulation)[6] is a model allowing the examination of effects of control options on deposition of sulfur and acidification of the soil. It was developed for use in South Eastern Asia, hence, is not directly applicable to Australia; however, by selecting regions of Asia with similar climatic conditions to South-East Queensland (where the coal-fire power plant is located), a comparison giving the magnitude of expected results can be obtained. Furthermore, RAINS-ASIA is a model specifically looking at the deposition of sulfur and its contribution to acidification over long distances. The factors extractable from this model for comparison are the deposition rates per unit of area.

Examining the stationary point sources and the climatic data for the different regions of South Eastern and Central Asia that the model addresses, the Guang Zhou province of China proved to be the most comparable, with a single stationary source emitting 24,800 tonnes of sulfur (similar to the emissions rate of 27,000 tonnes for the source examined in this validation) and climatic conditions similar to the region of interest.

The differences between the current model and the RAINS value at individual sites is due to RAINS incorporating only

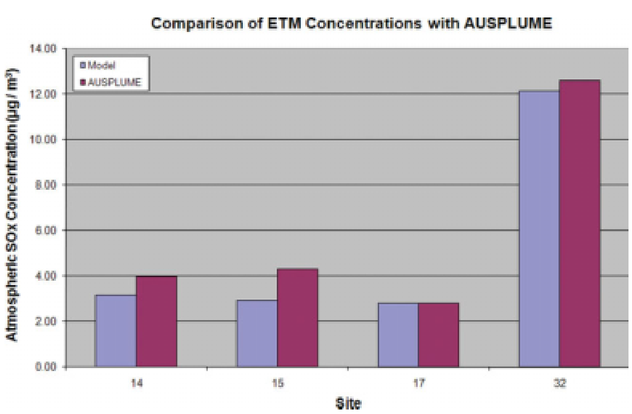

Figure 10. Comparison of atmospheric SOx concentrations from ETM with AUSPLUME.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table 4. Comparison of model with RAINS-ASIA—Annual Deposition

	Annual Deposition Rate (mg/m^2/yr)	Total Annual Deposition (t)	Percentage of Emissions (%)
Model	151–1695 (186 average)	6812	27.6
RAINS	170	6013	24.2

an average deposition over a large area (approximately 90 km × 90 km), whereas the current model examines deposition on a more local scale, with average values over the tank surface area (circles of radius 3–15 km for the sites of interest). The monitored sites are all in close proximity to the plant, which accounts for the higher deposition rate in comparison with the average. Comparing the overall average values, however, shows that across the whole area of interest, RAINS and the current model give very similar deposition rates (Table 4).

The comparison of the current model deposition rate with RAINS-ASIA shows that the results are quite close in terms of deposition. This result allows greater confidence in application of the model.

Discussion

The results and implications of this work are three-fold, which arises from the monitoring, the model, and the sustainability context. Firstly, the monitoring regime indicates that there has been a real increase in soil sulfur concentration over the period of monitoring around the power station. This is attributable to the emissions from the power station and the recent drought in the area (which has prevented washout). Since the time of this work, the area has received much higher levels of rainfall than the previous 5 yr, which may have brought the sulfur levels down again. Monitoring under the current regime has focused on vegetation uptake of emissions, rather than soil concentrations, with only irregular soil testing. This recent testing, however, indicates that there is useful data to be gained from soil testing—even if the interval between measurements is long. It is recommended that more testing be carried out to identify the effects of recent rainfall and to improve the model performance. The fact that monitoring has been undertaken represents a significant opportunity for further research in this unique context.

Second, the ability to model the emissions, deposition, and removal from soil by rainfall using the process approach allows the end use in sustainability metrics to be undertaken. Environmental data is very complex, so this work takes the approach of using the midpoint of soil deposition and subsequent soil concentration variation based on purely physical processes. Omitting the biological and biochemical influences of the receiving environment naturally causes some error and variability, however, inclusion of these exceedingly complex processes would belie the inherent error in prediction, thus, giving a false appearance of precision. In truth, the inclusion and perfect modeling of even a single site would require resources and analysis beyond the scope of any corporation or study because of the vast number of parameters in constant flux. Given that the available data does not support a more complex model and that the inclusion of only physical processes still allows validation within the limits of error, it is concluded that the omission of these processes is both warranted and valid. Furthermore, the ability to reduce data requirements for monitoring and modeling of environmental flows is useful from a cost and practicality perspective.

The model was fitted to the empirical data using variation of multiple parameters derived from the process modeling approach described. The key variables derived from the process approach were the control factors modellng runoff and permeability. The validation of the model based on data from a local power station and the comparison of results for deposition and atmospheric concentration with accepted existing models indicate that it is able to mimic environmental behavior within reasonable limits of accuracy for the desired application. The sensitivity assessment shows that the model is robust in response to variation of parameters and highlights that the parameters of highest impact are those factors, which affect the removal of sulfur from the soil. The particularly strong influence of the annual rainfall rate has significant implications for the future acidification of the soil in drought conditions and with the potential for decreasing annual rainfall in a future climate influenced by global warming. This factor could also be a strong influence when siting of a potential plant is considered, because the influence on soil may be mitigated under conditions of higher rainfall. The ultimate sink for any leached contaminants would be groundwater and surface water, which are not examined here due to the lack of historical data for validation, but this is an area needing further research.

In applying this model to the sustainability metrics system, excessive complexity would limit the usefulness of the system. The ETM requires a minimal number of parameters, but it would still take significant efforts to obtain the empirical data on soil runoff and permeability for each new site. The model could benefit from a further examination of soil classifications and topographical data to come to a more rigorous method of estimating the control factors for runoff and permeability from existing or remotely measurable data. The current model is also limited in the number of ‘‘sub-airshed tanks’’ that it uses, which could be increased if a greater number of monitoring sites were used. However, this would require a more extended tuning process for the model. If capacity for monitoring is limited, as is typically the case, then identification and selection of the most sensitive sites (as monitoring sites) would be recommended. From the perspective of monitoring the ultimate fate of emissions, it is recommended that future work aim to combine the more complex atmospheric and hydrological models currently in use, because this would hopefully provide greater accuracy and easier uptake in industrial applications.

As previously mentioned, the ETM was developed as a core element of a location-specific sustainability metrics methodology, and its key value is its usage in this context. Typical sustainability metrics do not incorporate emissions transport or key environmental factors, such as rainfall, which leaves them largely devoid of context (i.e., they become simply an indicator of technology performance, not local sustainability impact). These typical models represent the ‘‘loading model’’ of emissions, which has been shown here to not to reflect the actual situation. The nonlinearity of the response of the modeled soil sulfur concentration to step changes in emissions or other parameters supports the use of an ETM in sustainability assessment. If a directly proportional, linear response had been recorded for all parameters, it might be assumed that a loading-model system would be sufficient. However, a nonlinear response to emissions variation in particular denies the validity of loading models except for use in comparison of potential technologies. This finding throws the validity of purely technological performance-based sustainability metrics into question.

Conclusions

This article has described a combined atmospheric-hydrological model derived using a process approach to environmental transport modeling. A system of tanks, reactors, and pipes is used to create the model. The results of model verification and sensitivity analysis show that the model gives sound performance in regards to fitting the empirical data on soil sulfur concentrations. The development and verification of the model was made possible due to the availability of soil data across a 23-yr period, around an isolated coal-fired power station. Verification indicated that the environmental sulfur concentrations had risen because of the power station, but that the soil concentrations were largely dependent on annual rainfall, which had decreased in recent years, leaving an elevated level of soil sulfur.

The developed model allows local soil and climatic conditions to be incorporated, which is vital in assessing environmental impacts of emissions. This model was created in the context of a location-specific sustainability model, and the results of applying the model indicate that there is a need for this type of new approach to sustainability metrics. The ETM indicates a nonlinear response of soil sulfur to increases in power station emissions, which shows the limitations of one of the underlying assumptions of current sustainability metrics.

The ETM has a number of limitations which are recommended as potential areas of further research and development. The inclusion of ground and surface water sulfur concentrations and atmospheric and soil water chemistry would be of significant value. Furthermore, combining more complex models of groundwater and atmospheric transportation would likely result in improved accuracy.

Acknowledgments

The authors thank Tarong Power Station for providing data for this study and, in particular, special thanks for Mr Leigh Miller and Mr Frank Hodgkinson for their discussions on this topic.

Notation

α = model coefficient (Eq. 7)
μ = fraction surface water in sub-airshed
b = background concentration (μg/m^3)
c = concentration (μg/m^3)
$c_i/64$ = Molar concentration of sulfur in air in tank 'i' (μgmol/m^3)
c_1 = sub-airshed "1" sulfur concentration (μg/m^3)
c_r = rainwater sulfur concentration (μg/m^3)
c_s = soil sulfur concentration (μg/m^3)
c_{s0} = bulk soil sulfur concentration under ambient conditions (μg/m^3)
D = deposition = $u.c.FSA$ (μg/s)
E_i = emission rate (μg/s)
F = runoff factor
FSA = surface area of land forming the base of the tank (m^2)
G = permeability factor
k = Henry's law constant
K_L = runoff removal factor
K_P = permeation removal factor
M = total mass of sulfur (μg)
n_{air} = number of micro moles of air in 1 m^3 $\approx 44.6 \times 106$ (at 273 K and 1 atm)
NF_i = natural flux in = $b.v.SA_1$ (μg/s)
NF_o = natural flux out = $c.v.SA_2$ (μg/s)
P = Partial pressure of sulfur in air
q_r = rainfall rate (m^3/s)
$q_{r(t)}$ = annual rainfall for a given year (t) (m^3/yr)
$q_{r(N)}$ = historical average annual rainfall (m^3/yr)
r_p = rate of removal by plants (μg/m^2)
r_s = rate of removal by reaction (μg/m^2)
SA_i = vertical surface area of airshed 'tank' i (m^2) (airsheds counted radially out from the centre)
u = deposition velocity (m/s)
v = wind velocity (m/s)
t = time (s; used for calculation) or (yr; used for reporting)

Literature Cited

1. Wang X, Carmichael G, Chen D, Tang Y, Wang T. Impacts of different emission sources on air quality during March 2001 in the Pearl River Delta (PRD) region. *Atmos Envir*. 2005;39:5227–5241.
2. Migon C, Caccia J-L. Separation of anthropogenic and natural emissions of particulate heavy metals in the western Mediterranean atmosphere. *Atmos Envir Gen Top*. 1990;24:399–405.
3. Thunis P, Cuvelier C. Impact of biogenic emissions on ozone formation in the Mediterranean area—a BEMA modelling study. *Atmos Envir*. 2000;34:467–481.
4. Tao Z, Larson SM, Williams A, Caughey M, Wuebbles DJ. Area, mobile, and point source contributions to ground level ozone: a summer simulation across the continental USA. *Atmos Envir*. 2005;39:1869–1877.
5. Diniz da Costa JC, Pagan RJ. Sustainability metrics for coal power generation in Australia. *Trans IChemE*. 2006;84(B1):1–7.
6. IIASA. RAINS-ASIA User's Manual. Laxemburg, Austria: IIASA, 2001.
7. NPI. National Pollutant Inventory Emissions Data. Available at www.npi.gov.au. June 23, 2006.
8. Larssen T, Knudsen S, Bruteig I, Aarrestad PA, Høgåsen T, Kinn SJ, Engen S, Johnsen S. Environmental impact factor for emissions to air: a tool for prioritizing emission-reduction measures based on environmental impacts and benefits. In: 8th SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production 2006. Abu Dhabi, United Arab Emirates: Society of Petroleum Engineers; 2006.
9. Berden M, Nilsson SI, Rosen K, Tyler G. Soil Acidification—Extent, Causes and Consequences. Solna: National Swedish Environmental Protection Board Research Secretariat, 1987.
10. Cresser MS. The critical loads concept: milestone or millstone for the new millennium? *Sci Tot Envir*. 2000;249:51–62.
11. Likens GE, Bormann FH, Hedin LO, Driscoll CT, Eaton JS. Dry deposition of sulfur: a 23-year record for the Hubbard Brook Forest ecosystem. *Tellus B*. 1990;42:319–329.
12. McLellan B. Location-Specific Sustainability Metrics for Hydrogen Energy Systems. PhD Thesis. Queensland, Australia: University of Queensland, 2007.
13. De Nevers N. Air Pollution Control Engineering. 2nd ed. Sydney: McGraw-Hill, 2000.
14. Potter TD, Colman BR. Handbook of Weather, Climate, and Water: Atmospheric Chemistry, Hydrology, and Societal Impacts. Hoboken, NJ: Wiley-Interscience, 2003.
15. Seinfeld JH, Pandis SN. Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. New York, NY: Wiley, 1998.
16. IIvonen P, Kamari J, Posch M. Modelling the chemical response of a moderately acidified catchment in southern Finland to decreased sulphur deposition. *Aqua Fennica*. 1993;23:235–249.
17. Duan L, Xie S, Zhou Z, Ye X, Hao J. Calculation and mapping of critical loads for S, N and acidity in China. *Water Air Soil Pollut*. 2001;130:1199–1204.
18. Hettelingh JP, Posch M, De Smet PAM, Downing RJ. The use of critical loads in emission reduction agreements in Europe. *Water Air Soil Pollut*. 1995;85:2381–2388.
19. Quilchano C, Haneklaus S, Gallardo JF, Schnug E, Moreno G. Sulphur balance in a broadleaf, non-polluted, forest ecosystem (central-western Spain). *For Ecol Manage*. 2002;161:205–214.

20. BOM. Australian Bureau of Meteorology Website. Available at www.bom.gov.au. Accessed June 2005.
21. Gilmour J, Mayhew B, Ayers G, McCullough R, Borgelt B, Harris R, Neilson L, Thinee J, MacLennan R, Williams D. Final Report of Mt Isa Mines Limited Panel Assessment Study. Mt Isa: MIM, February 2001.
22. Plenderleith RW. Tarong Crop and Forestry Study. Brisbane, Queensland: Electricity Commission—Generation Technology Department (Environmental Section), February 1989.ETM88/055.
23. Woodward-Clyde. 2 × 420MW Coal Fired Unit Extension at Tarong Power Station—Draft Review of Environmental Factors. Brisbane, Queensland: Tarong Energy, June 1998. A3201213/0002.2.
24. EPA Victoria. AUSPLUME Gaussian-plume Dispersion Model Technical User Manual. Melbourne, Australia: Environmental Protection Authority Victoria, 2000.
25. Hurley P. The Air Pollution Model (TAPM) Version 2. Part 1: Technical Description. Melbourne, Australia: CSIRO, 2002.
26. Katestone. Selection of Suitable Fine Dust Monitoring Sites Around Tarong Power Station. Brisbane, Queensland: Katestone Environmental, September 2005.

Manuscript received Mar. 19, 2009, and revision received May 7, 2009.