A New Approach to Acidification in LCA

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ABSTRACT

Any air emission is classified as acidic when the release of that emission causes the resultant precipitation to have a higher hydrogen ion concentration — $[H^+]$ — than that for normal rainwater. The treatment of acidifying airborne emissions in life cycle assessment has, to date, consisted principally of globally aggregated inventory data. As such their use in calculating $[H^+]$ is inappropriate since acidification is a regional rather than a global effect. This paper suggests a different approach, in which standard chemistry calculation techniques are used to determine $[H^+]$ at a regional level, accounting for both variations in acid mix and local precipitation.

INTRODUCTION

Automobiles are highly complex machines and are built using hundreds or even thousands of components. The systems that produce these components can be based in one country or region but are frequently spread over several countries, sometimes even over more than one continent. Figure 1 shows a breakdown of a simple vehicle into its major components.

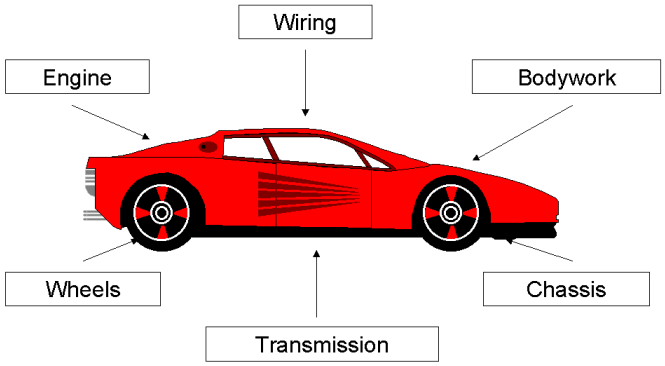

Figure 1 Major components of a vehicle.

For example, in the European Union engines manufactured by BMW (in Germany), PSA-Citroën (in France) and Ford (in the United Kingdom) are exported all over Europe, for use both by the maker's own vehicle manufacturing plant and by other rival manufacturers who prefer to outsource for economic or other reasons. Complete vehicles are also exported worldwide, thus further increasing the geographical scope of any subsequent environmental study.

Life cycle inventory (LCI) is a useful tool for characterizing these systems in terms of their gross (i.e. cradle-to-gate) energy and raw materials consumption and their waste streams of solid, liquid and gaseous emissions. Knowledge of these gross parameters can help us in quantifying potential contributions to global effects. For example, we can apply the carbon dioxide equivalent potentials issued by the Intergovernmental Panel on Climate Change (IPCC) to a detailed air emission inventory to determine the total global warming potential.

It is tempting to think that these gross air emission inventory results can also be applied to analysis of airborne acidification. However, doing so without applying some commonsense can result in precisely determined, yet meaningless, results. The main reason for this is that we must appreciate fully what our inventory data are describing. As we have already stated, an entire vehicle production system can span several continents and therein lies our problem. Airborne acidification is not a phenomenon that can be treated in the same way as global warming, because the effects of acidification are regionalized. Therefore, if we wish to conduct a meaningful analysis of acidification we must re-evaluate our air emissions inventory data set so that we have information at a regional level.

Fortunately, the level of detail required in conducting an inventory study allows us, with comparative ease, to make such a breakdown as the information necessary has already been obtained. The rest of this paper discusses the factors that need to be considered in any discussion of airborne acidification, using a re-evaluation of the results of an existing LCI study conducted on a vehicle as an example.

ACID RAIN

When we talk about airborne acidification it is important to set out just what exactly is meant by this term. Pure water has a value for $[H^+]$ of 1×10^{-7} mol/l. However, atmospheric carbon dioxide reacts with the water vapour in clouds to form aqueous solutions of carbonic acid. The concentration of this dilute carbonic acid is determined by the solubility of carbon dioxide, which in turn is dependent on the partial pressure. Using Henry's Law we can determine that at sea level and at a pressure of one atmosphere the solubility of carbon dioxide is approximately 7.0×10^{-6} mol/l. Since 1 mole of carbon dioxide reacts to produce 1 mole of carbonic acid, the molar concentration of the aqueous carbonic acid solution is also 7.0×10^{-6} mol/l.

If we use standard chemistry calculation techniques for determining $[H^+]$ from the acid dissociation constants, we will eventually find that after all dissociations have been considered, $[H^+]$ is 1.64×10^{-6} mol/l. This corresponds to a pH value of 5.78. Rainwater is therefore naturally acidic. When determining hydrogen ion concentrations due to air emissions, emissions of carbon dioxide are not considered since the solubility calculation above limits the total amount of carbon dioxide that is absorbed. However, the addition of other air emissions further increases acidity beyond this level, so what is really meant by acid rain is rain that has a pH below 5.78 (or $[H^+]$ greater than 1.64×10^{-6} mol/l).

ACIDIFICATION CALCULATIONS

In any determination of hydrogen ion concentrations there are a number of factors that need to be accounted for. These are:

- The nature of the acids formed
- Multiple dissociation routes
- Precipitation characteristics

THE NATURE OF THE ACIDS FORMED

Not all acids are the same. Essentially there are two types of acid dissociation, 'strong' and 'weak' and these terms are also applied to the acids. Strong acids dissociate completely and almost instantaneously in contact with water. Furthermore, this complete dissociation takes place regardless of the prevailing $[H^+]$. For weak acids, on the other hand, dissociation is affected by the existing $[H^+]$. It is important, therefore, that we distinguish between these two types of acid and treat them accordingly. The detail contained within an inventory enables us to adequately distinguish between the various air emissions.

MULTIPLE DISSOCIATION ROUTES

Sulphur dioxide is peculiar in that it can form two distinct compounds, sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4), depending upon the conditions. This presents a problem because these two acids exhibit distinct and very different characteristics. Sulphuric acid has two dissociations, forming HSO_4^- and SO_4^{2-} respectively. The first of these is strong and therefore takes place completely. The second dissociation is however weak. Sulphurous acid also has two dissociations, in this case forming HSO_3^- and SO_3^{2-} respectively. Both of the sulphurous acid dissociations are weak. When we consider emissions of sulphur dioxide we must therefore consider formation of both sulphurous and sulphuric acid.

PRECIPITATION CHARACTERISTICS

The one factor that we have not yet talked about is the quantity (i.e. volume) of precipitation into which the air emissions are absorbed. This is highly important, as it is this factor that determines the molar concentrations of the acidifying air emissions and hence the final value of $[H^+]$. We must therefore refer to historical precipitation data when considering what the likely precipitation in any given location may be. Historical data obtained over a number of years will also indicate extremes (i.e. maxima and minima) as well as average precipitation for the period over which the records extend. We also need to consider where released emissions are likely to end up. Again, historical data will help, especially with regard to annual emission releases, however individual releases (e.g. of a catastrophic nature, such as Seveso, Bhopal or Chernobyl) are subject to the exact weather conditions that exist at the time of the release.

CASE STUDY

In a project conducted to investigate the life cycle inventory for the production of a small, non-catalyst equipped, three-door vehicle [1, 2], production plant in both Italy and China were analysed. The total air emissions for the vehicle manufactured and driven in Italy are summarized in Table 1. It should be noted that the aim of the study was to provide inventory data for the systems under consideration: it was not concerned with describing acidification effects due to air emissions.

The use phase accounts for the vehicle being driven a total distance of 100,000 km over a period of five years. In the same way that it is possible to separate out the production and use phases of the inventory, we can also further isolate those individual components production processes i.e. engine production, chassis production etc. The advantage of refining our data in this manner is that we also automatically demarcate the geographical regions in which each process takes place.

Table 1.
Gross air emissions (in kg) associated with the production and use of a small 3 door vehicle in Italy.

Air emission	Production	Use	Total
Dust	3.30	14.00	17.30
CO	12.00	151.00	163.00
CO_2	1800.00	18000.00	19800.00
SO_x	14.00	70.00	84.00
NO_x	7.90	191.00	198.90
Hydrocarbons	5.50	195.00	200.50
Methane	3.50	3.00	6.50
HCl	0.09	0.01	0.10

Using the detail inherent in the LCI study, it is possible to construct a new table, which shows the countries/regions in which the air emissions listed in Table 1 are actually released. The strength of this new way of presenting data is that it may readily be applied to the study of other regional effects besides acidification. Table 2 shows the re-evaluated data.

Table 2.
Gross air emissions (in kg) associated with the production and use of a small 3-door vehicle in Italy, showing country of origin.

Country	HCl	NO_x	SO_x
France	0.00	0.04	0.12
Germany	0.00	0.02	0.05
Italy	0.05	195.80	79.80
United Kingdom	0.05	3.03	4.03
Total	0.10	198.90	84.00

It is not surprising to note that, in this example, the majority of the acidifying air emissions are released in Italy. If instead the same vehicle was exported to and driven in the United Kingdom, then the geographical distribution of the acidifying air emissions would be as shown in Table 3. Since these emissions totals are the quantities released due to the production and use of the vehicle over five years, we need to account for this time period in our acidification calculations.

Table 3.
Gross air emissions (in kg) associated with the production (in Italy) and use (in the United Kingdom) of a small 3 door vehicle, showing country of origin

Country	HCl	NO_x	SO_x
France	0.00	0.04	0.12
Germany	0.00	0.02	0.05
Italy	0.03	5.74	10.89
United Kingdom	0.03	191.20	60.54
Total	0.06	197.00	71.60

It has long been recognized that air emissions released in the United Kingdom are responsible in part for the acid rain falling on Scandinavia. We can see from Table 3 that our vehicle is responsible for the emission of 30 g of HCl, 191.2 kg of NO_x and 60.54 kg of SO_x in the United Kingdom. Let us consider the effect of these emissions if they were to fall on Sweden. The surface area of Sweden is 449,964 km^2, and for simplicity we will consider the effect of one million vehicles with the aforementioned characteristics operating over a five-year period in Britain. Table 4 shows the annual precipitation data for four Swedish towns over a corresponding timescale.

Table 4.
Historical precipitation data (in mm) for four towns in Sweden.

Town/Year	1986	1987	1988	1989	1990	Total
Lund	633	661	693	527	629	3143
Kiruna	460	526	491	522	494	2493
Stensele	497	573	617	526	538	2751
Stockholm	620	474	615	385	644	2738

If we assume that the precipitation that fell across the whole of Sweden is similar to that which fell over Lund, then the resultant precipitation would have a pH of 5.28 if sulphurous acid was formed, or a pH of 5.21 if sulphuric acid was formed. However, if the rainfall total for Kiruna is more appropriate, then the rainfall will be even more acidic, since the same quantities of the various air emissions are now absorbed into a smaller volume of water (the corresponding pH values would be 5.21 and 5.15 respectively). Clearly, as all values are below that for normal rainwater, pH 5.78, then this can truly be considered as ‘acid rain’. In reality any such analysis would use precipitation data obtained over a much larger period, and would account for maxima and minima.

Although only three types of acidifying emissions are shown here this method can be applied to any number of acidifying emissions. It should be emphasized that the figures presented in Tables 1-4 should be regarded as illustrative values. Furthermore, the authors recognize that any detailed acidification analysis would not assume that precipitation falls uniformly across an entire country. The main aim of the example presented here is to illustrate the principles behind this new approach to acidification analyses in LCA.

CONCLUSION

Acidification is a regional effect and any attempt to characterize this effect should reflect this fact. The detail inherent in any LCI study provides an excellent basis for this. Crucial to this approach is the identification of the geographical regions in which the acidifying air emissions are released. When this information is coupled

with historical precipitation data, then it is possible to conduct a more meaningful analysis of airborne acidification than is currently undertaken.

REFERENCES

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