

CHAPTER 2

LITERATURE REVIEW

2.1 Substance Flux Analysis

Substance Flux Analysis (SFA) is an environmental accounting tool based on a physical input-output analysis, or the mass balance principle. It is a tool which can be used to analyze the societal metabolism of substances and to evaluate how products are introduced into, utilized within, and disposed from a system. The technique can be used to identify causes of pollution problems associated with the flows of specific substances in a given time frame and region, and subsequently for considering possibilities for preventing pollution. (Baccini and Brunner, 1991; Guinee *et al.*, 1999; Kleijn *et al.*, 1999; Bouman *et al.*, 2000 and Barr Engineering Company, 2001). Substances analysed using the SFA method can be elements, chemical compounds or a group of chemical compounds (Lassen and Hansen, 2000).

The SFA technique is useful for supporting environmental policy by enabling policy makers to trace the origins of pollution problems and to evaluate appropriate means for the management of potentially hazardous substances by society.

2.1.1 The principle of the substance balance

According to the principle of conservation of mass, recognised since the 18th century, the total mass of a substance is always constant. This principle can be rephrased in terms of a simple mass balance: input equals output plus stock. In the case of chemical compounds that are composed of more than one element, chemical, biological or thermal processes may lead to their formation and degradation (Lassen and Hansen, 2000). The mass balance principle can therefore be further rearticulated as the basis for SFA as shown in equation 2-1:

$$\text{INPUT} + \text{FORMATION} = \text{OUTPUT} + \text{DEGRADATION} \quad (2-1)$$

These entities must be quantified in the context of a system which is precisely defined in time and space. Over a given period of time, for example, a substance entering the system may have not been fully used up, hence resulting in development of a stockpile of the substance - referred to as “accumulation” (Kleijn *et al.*, 2000 and Lassen and Hansen, 2000). By incorporating a time boundary, the substance balance can be expressed as equation 2-2:

$$\text{INPUT} + \text{FORMATION} = \text{OUTPUT} + \text{DEGRADATION} + \text{ACCUMULATION} \quad (2-2)$$

If $\text{INPUT} > \text{OUTPUT}$ the substance will accumulate and stocks will be formed within the system. If $\text{INPUT} < \text{OUTPUT}$, there will be a negative accumulation and the stocks in the system will become depleted.

Equations (2-1) and (2-2) can be articulated in a number of ways depending on the system they aim to describe. If the purpose is to assess the consumption of a product in a region, for example, the expression will become:

$$\text{IMPORTS} + \text{REGIONAL PRODUCTION} = \text{EXPORTS} + \text{CONSUMPTION} \quad (2-3)$$

Equations (2-1) to (2-3) describe substance balances in the simplest form. They can become more sophisticated depending on the level of detail desired in analysis.

2.1.2 General framework for the SFA approach

A methodology for the SFA framework has recently been discussed among European SFA practitioners and has been published in Brunner and Rechberger (2003). A number of recent examples of the SFA approach, mostly from European countries, are listed in Table 2-1. To date little experience in the use of the SFA approach exists in developing countries.

Table 2-1 : Research studies using Substance Flux Analysis and related approaches

Title / Study area	Specific substances	References
Dynamic Substance Flow Analysis: The delaying mechanism of stocks, with the case of PVC in Sweden	PVC products.	Kleijn <i>et al.</i> (1999)
Dynamic models for managing durables using a stratified approach: The case of Tunja, Colombia	Furniture in private households	Binder <i>et al.</i> (2001)
Material flows and economic models: An analytical comparison of SFA, LCA and Partial Equilibrium Models	Approach for all substances	Bouman <i>et al.</i> (1999)
Analysis of the paper and wood flow in The Netherlands	Paper and wood	Hekkert <i>et al.</i> (1999)
An analysis of variables influencing the material composition of automobiles	Automobiles	Kandelars <i>et al.</i> (1998)
Evaluation of risks of metal flows and accumulation in economy and environment	Cadmium, copper, lead, and zinc	Guinee <i>et al.</i> (1998)
New estimate of the amount of cadmium in Denmark	Nickel-Cadmium batteries	COWI and Drivsholm (2001)
Substance Flow Analysis of mercury in products	Mercury	Barr Engineering Company (2001)
The contemporary European copper cycle: Introduction	Copper	Graedel <i>et al.</i> (2002)
The contemporary European copper cycle: The characterization of technological copper cycles	Copper	Graedel <i>et al.</i> (2002)
The contemporary European copper cycle: 1 year stocks and flows	Copper	Spatari <i>et al.</i> (2002)
Integrated chain management by applying Substance Flow Analysis in the Flemish region of Belgium	Heavy metals	Holderbeke and Timmermans (2002)
Predicting future emissions based on characteristics of stocks	Waste	Voet <i>et al.</i> (2002)
Cadmium in the European community: A policy-oriented analysis	Cadmium	Voet <i>et al.</i> (2002)

A proposed general framework for SFA consists of four steps (Lassen and Hansen, 2000 and Brunner and Rechberger, 2003): 1) goal and system definition; 2) system analysis; 3) inventory, evaluation of data, and modeling; and 4) interpretation of the results:

- (1) Goal and System Definition: the overall goal of SFA is to provide a comprehensive picture of the flow of a substance through a region's society based on fundamental considerations relating to risk minimization. The SFA system is defined by boundaries in space and time which are established as the first step of the study. It is not uncommon for the definition and interpretation of goals to be modified following the system analysis step.
- (2) System Analysis: the whole system is considered thoroughly in this phase. All types of transport and process with potential impacts on the flow of the substance through society are identified. During this phase the data requirements and degree of accuracy needed are determined. It should be noted that the flow system established in this phase is seldom perfect. Certain aspects will probably have been overlooked and other types of transport or process identified as essential may turn out to be unimportant. In practice system analysis is an iterative process through which the system is modified continuously as more knowledge is obtained. The outcome of this phase may affect both the goal and system definition and the inventory.
- (3) Inventory, Evaluation of Data, and Modeling: this phase begins with collection of accessible data consisting of statistical information about the production, import and export of relevant raw materials, semi-manufactured goods and finished products. Monitoring data concerning waste streams is also required. A strategy is then devised for continued collection of data. During the inventory the pieces of the puzzle (the individual data sets) are put together to give an overview. The figures will often not correspond precisely

and there will be need for more detailed evaluation of the data to find out the reasons for this.

- (4) Interpretation of the Results: the basic interpretation should be reported with a discussion of the flow chart derived from the study and the cross-checks made. In reality much of the data collected for an SFA is so uncertain that it has little value until it has been cross-checked. The main sources of emission of the substance to the environment and losses to waste are identified, together with emissions of potential importance where more data is needed.

Although the principles of the SFA approach are very simple, the practical procedures are seldom so straightforward. The reality is often complex and acquiring the necessary data can be very difficult. The data is seldom 100% accurate and is usually subject to varying degrees of uncertainty (Lassen and Hansen, 2000 and Barr Engineering Company, 2001). The procedures used in a particular case will depend on the patterns of application and flow of the chemical substances to be analyzed, the purpose of the analysis, the level of detail required, and the level of reliability which is necessary.

2.1.3 Benefit of the SFA approach

- (1) SFA informs environmental policy-maker *a priori* about the likely main source of hazardous substances, and it can be used for prioritized management actions in an area which contributes inputs to P and Cd sensitive lakes.
- (2) SFA helps in the development of alternative substance flow control strategies. These options include banning the use of some selected substances in some goods, limiting the concentration in goods (e.g., limiting the Cd concentration in phosphate fertilizer), increasing the recycling rate of some goods (e.g., NiCd in batteries), and improving the level of treatment in waste treatment processes. Strategies will consist of different combinations of options for each element of concern.

- (3) SFA is a tool to identifying pollution problems and assessing the impacts of different potential solutions. A key advantage is the speed at which feasible and non-feasible options can be technically scanned.
- (4) SFA enables unexpected flows and emissions to be anticipated, and also allows accumulation of stocks in the economy or environment which may cause problems in the future to be identified.
- (5) Before cost-effective control measures can be targeted, we must identify critical source areas vulnerable to P and Cd loss from a catchment, account for variations in the catchment response to protection measures which are implemented, and ultimately aim to predict the response of affected waters.

2.1.4 The limitation of the SFA approach

Although SFA appears to be useful tool and there is relatively good data available about its use, it is also subject to certain limitations (Baccini and Brunner, 1991; Bouman *et al.*, 2000; Lassen and Hansen, 2000 and Binder *et al.*, 2001):

- (1) Real life situations, which SFA aims to model, are often complex. The data available is seldom 100% accurate, if available at all, and is subject to varying degrees of uncertainty. In most cases, only an “order of magnitude” estimate can be given for substance fluxes.
- (2) A certain degree of estimation has been necessary in the study. It is often difficult to decide which of the available data it is appropriate to use. Given the limited information available for the SLC, information from other areas has been adopted. Though every effort has been made to use the most suitable data, information from “dissimilar” catchments and conditions will inevitably have been adopted in some cases.
- (3) In reality, certain products will remain in use for many years. However, it is sometimes necessary to estimate the amount of substances contained in products which may have been purchased or

installed many years ago but which have become potential sources of P and Cd release over the period of analysis. Thus, the life span of long-lived products can complicate the calculation of annual consumption of the substances under analysis.

- (4) The SFA technique is based only on the information available. A major problem in considering substance balances in developing countries is a lack of reliable data. Furthermore, this technique does not take into account the economic value of flows and trade-offs, and thus cannot be used for an analysis of economic effectiveness or the economic consequences of policy instruments such as taxes or subsidies.

2.2 Phosphorus

Phosphorus (P) is the principal substance causing eutrophication in lakes and water bodies. P can enter the water environment in three ways:

- (1) Natural sources: some P originates naturally by weathering of rocks. Geology can play an important part in determining the P economy of a region. Inorganic P constituents in mineral soils are generally classified into two groups, namely calcium phosphates and iron and aluminum phosphates (Dormaar, 1972). The P content in the earth's crust is relatively low at around 1,100-1,200 mg/kg (Tisdale *et al.*, 1985). Likewise, the total P content of mineral topsoil is relatively low at 50-1,100 mg/kg (Brady, 1990), giving rise to issues relating to poor crop yields in agricultural systems where P is a limiting factor.
- (2) Atmospheric inputs: in some situations, atmospheric inputs of P may be significant. The range of atmospheric P input varies from 5 to over 100 kg/km²/y. It is likely that humans have a direct influence on the magnitude of atmospheric inputs of P, and the lowest values are found in areas remote from civilization (Ahl, 1988).
- (3) Anthropogenic sources: P loss rates from catchment vary widely depending on population density and agricultural intensity.

Loss of P and other nutrients from the land to rivers or lakes depends not only on hydrological events but also human activities. Compared with a river, a lake can retain nutrients for a much longer period and thus nutrients are more readily available for uptake by aquatic plants. Excessive aquatic plant growth can result in reduction of the clarity of water in the lake and the death of fish (Porter, 1975). At the present time it has been found that water quality in some areas of the SLC does not meet the National Water Quality Standard including the standard for total phosphorus (PCD, 2000). Nutrients and toxic metals carried in runoff from agricultural fields and flushed into streams and lakes, as well as eroded soil particles, contribute to low water quality. Sources and P loads to the SLC are summarized in Table 2-2 (EmSong, 1999a). Porter (1975) identifies the principal sources of P contribution to lakes as: 1) precipitation and other atmospheric fallout; 2) effluent from municipal sewage treatment plants; 3) industrial and domestic wastes; 4) inputs from non-sewered households such as household laundry detergents; 5) runoff from urban and cultivated areas and forest soils; and 6) application of P to land, for example as phosphate fertilizer and compost.

Table 2-2 : Sources and entry of phosphorus to the Songkhla Lake Catchment

Source	P (t/y)	Trend
Urban areas	60	Rapid increase until WWTPs are in operation
Industries	100	Rapid increase until WWTPs are in operation
Rural areas	165	Increasing
Farmland rice	170	Increasing
Farmland rubber	20	Moderate rate of increase
Cow and buffaloes	20	Moderate rate of increase
Pig farming	110	Increasing due to intensive pig farming
Chickens & duck farming	40	Unchanged
Fish aquaculture	14	Increasing rapidly depending on market
Shrimp ponds discharging to lake	11	Increasing rapidly depending on market
Total discharge to the lakes	710	

WWTP: Wastewater Treatment Plant.

Source: Emsong, 1999a.

2.2.1 Phosphorus loss from agricultural soil

The potential loss of P from agricultural land is dependent on several factors. The loss of P from agricultural fields can be divided into three categories of event (Lennox *et al.*, 1997 and Lory, 1999): 1) Flash losses of soluble P soon after application of manure or fertilizers. Under such circumstances the concentration of soluble P in the runoff can be more than 100 times higher than normal. 2) Slow natural leakage losses of soluble P from all soils into surface runoff. Research from other states indicates that soil tests for P were developed to help estimate phosphate fertilizer requirements for crops. 3) Under conditions where runoff water gains sufficient energy to cause soil erosion, the amount of P lost from fields increases dramatically.

2.2.2 The effect of phosphorus losses from agriculture

Farmers regularly apply fertilizer containing phosphorus as well as nitrogen and potassium to crops to increase yield. P can attach to particles of soil or manure which are eroded by water and enter a stream. Efforts to preserve water quality must therefore focus on prevention of this process. As nutrient concentrations increase, surface water quality is degraded through the process of eutrophication. The following symptoms characterize changes in surface water quality as nutrient concentration increases: 1) increased algal growth; 2) reduced water quality; 3) water treatment problems including odor and bad taste, increased filtration costs, and disinfectant byproducts with potential human health effects; 4) reduced oxygen levels in water; 5) impacts on fisheries; 6) fish mortalities; and 7) toxins from cyanobacteria (blue-green algae) which can affect human and animal health (Lory, 1999). Similarly, nutrient levels in surface water often restrict the growth of aquatic plant species. P is often the limiting element and its control is of prime importance in reducing the accelerated eutrophication of freshwaters such as lakes and rivers (Sharpley and Rekolainen, 1997 and Lory, 1999). Definitions for the trophic status of bodies of fresh water based on P concentration are shown in Table 2-3.

Table 2-3 : The characteristics of trophic levels in fresh water

Trophic status	Definition and characteristics
Oligotrophic	Poorly nourished, clear waters with limited sediment and biological activity. Total P concentration < 10 ppb.
Mesotrophic	Intermediate productivity and clarity. Total P concentration 10 to 25 ppb.
Eutrophic	High nutrient content. Potential water treatment problems with taste and odor. Total P concentration 25 to 100 ppb.
Hypereutrophic	Highly productive, murky waters. Can support cyanobacteria that may produce toxins. Total P concentration > 100 ppb.

Source: Jones and Knowlton, 1993.

The risk of P loss is determined by soil properties (plant available and total P content, organic matter content, P buffer capacity, depth, slope, texture, structure, hydrological features, pH, temperature etc), cropping features (extent of ground cover, type of crop, rate of growth and degree of root proliferation), the nature of the fertilization program (type and amount of fertilizer and manner and timing of applications) and by soil management regime (Sibbesen and Sharpley, 1997).

2.3 Cadmium

Cadmium (Cd) is a highly toxic metal. Cd found in soils originates from both natural and anthropogenic sources. Natural sources include underlying bedrock or material transported from bedrock, eg by erosion or physical transport, whereas anthropogenic input of Cd into soils occurs from atmospheric deposition and application of sewage sludge, manure derived from animal feed containing phosphate, and phosphate fertilizer application (Christensen and Tjell, 1983; Hovmand, 1983; Tjell and Christensen, 1992; OECD, 1994 and Guinee *et al.*, 2000). Cd is also found in certain manufactured goods, for example as a sacrificial corrosion protection coating, as a stabilizer in PVC, as a yellow pigment, and in microelectronic components and storage batteries (Jedvall, 1983).

Cd loadings on land may be transported to humans via the food chain and ingestion of the final crop and meat products (Andersson, 1983; Sommers and Sutton, 1986). Foods known to be sensitive to Cd uptake include grain, cereals, potatoes, root vegetables and leafy vegetables (Meeus *et al.*, 2001). Elevated Cd concentration

levels in wheat, some root crops, seafood and meat products have been reported (Baccini and Brunner, 1991; NSW EPA, 2000). The Cd content of grain grown in an unpolluted area was approximately 0.04 mg Cd / kg dry matter and may be higher in more polluted areas (Christensen and Tjell, 1983). According to the Provisional Tolerable Weekly Intakes (PTWI) specified by the WHO, dietary intake of Cd should not exceed 60-70 µg/day (OECD, 1994). Controls on the use of Cd to prevent its dispersal (for example by banning certain activities and uses), increased recycling of concentrated sources of Cd (eg NiCd batteries) and limits to Cd contamination in phosphate fertilizers are necessary to prevent future human health and eco-toxicity problems (Baccini and Brunner, 1991).

2.3.1 Cd contamination in soil

Cd-contaminated soils can be classified into three separate categories based on their relative impact on human health and the environment, namely cultivated soils, uncultivated soils and controlled landfills (NUS, 1987; Eggenberger and Waber, 1998).

The immobile Cd present in cultivated soils under normal conditions can become more mobile under certain conditions such as increased soil acidity. (Andersson, 1983 and Christensen and Tjell, 1983). Inputs of Cd into agricultural soils originate from atmospheric deposition, phosphate fertilizers (superphosphates with a high Cd content), manure and municipal sludge, and trans-boundary pollution (Tjell *et al.*, 1981; Hovmand, 1983 and Guinee *et al.*, 2000). The input of Cd into cultivated soils was generally found to be higher than the loss from crop removal, erosion and leaching (Loganathan and Hedley, 1997).

In uncultivated soils Cd does not generally affect human health as it does not enter the food chain readily, except under the rare circumstances of indirect transfer from uncultivated soils to cultivated soils via airborne or water transport.

Cd in controlled landfills is virtually immobile. As well as functioning as a waste disposal site to meet its designed function, a landfill site can also degrade or transform most organic substances into different forms. In the case of persistent chemical substances such as Cd, landfill can be regarded as a form of storage from

which these substances can slowly disperse into the environment through leaching. Cd is found in landfills in the form of cadmium sulfide, which is fairly stable and will not move into groundwater as long as conditions remain anaerobic (Lassen and Hansen, 2000). However, Cd in products placed in landfills could be released to the environment by: 1) losses to the atmosphere through daily, intermediate or final cover; 2) release via landfill gas vented directly to the atmosphere, if it has not passed through a flare or been burnt to generate energy; and 3) via collected leachate disposed of at a wastewater treatment pond. Evidence indicates that Cd release occurs via all of these avenues, with the possible exception of release through cover. Even placement of daily cover appears to significantly reduce or prevent Cd release to the air (Lassen and Hansen, 2000).

2.4 Key Products containing P and Cd contaminants

2.4.1 Phosphate fertilizers

Phosphate fertilizers have led to a significant increase in the Cd content of many agricultural soils because they are produced from phosphate rock, in which Cd is a common contaminant. The use of Cd-containing fertilizers is frequently cited as the primary reason for the increase in the Cd content of soils over the past 20 to 30 years in Europe. European fertilizers were found to be contaminated with Cd at a level of about 60 mg/kg of P₂O₅ (Davister, 1996). It was reported that at least 80% of Cd impurities contained in phosphate fertilizers applied to soil may remain in the soil (Camelo, Miguez and Marban, 1997 and Taylor, 1997). However, Cd concentration in such fertilizers can vary widely depending on the origin of the phosphate raw material (Alloway, 1995). Average P₂O₅ and Cd contents of chemical fertilizer produced from phosphate rocks are summarized in Table 2-4.

The Cd content of phosphate rock varies greatly, ranging from less than 5 mg/kg for rock from Kola to almost 100 mg/kg for rock from Nauru and as high as 300 mg/kg for rock from the Western USA (Davister, 1996). Single superphosphate fertilizer contains essentially all of the Cd present in the phosphate rock from which it is manufactured (Syers and Cisse, 2001). In several countries limits for the allowable content of Cd in phosphate fertilizers have been set and these are shown in Table 2-5.

Table 2-4 : Average P₂O₅ and Cd contents of main commercial phosphate rocks

Phosphate rocks	Total P ₂ O ₅		Cd contents	
	(%)	ppm/total	ppm/P ₂ O ₅	ppm/P
1. Igneous origin				
Kola	39	<5	<13	<30
Pharlaborwa	37	<5	<13	<30
2. Sedimentary origin				
Florida	32	7.5	23	54
Jordan	33	<10	<30	<70
Khouribga	32-33	15	46	106
Syria	31	16	52	119
Algeria	29	17.5	60	138
Egypt	27	20	74	170
Bu-Cra	34	34	100	229
Nahal Zin	31	31	100	229
Youssoufia	33	40	121	277
Gafsa	29	40	137	315
Togo	37	60	162	371
North Carolina	30	50	166	381
Taiba	37	75	203	464
Nauru	37	90	243	530

Source: Davister, 1996.

Table 2-5 : Allowable Cd contents in phosphate fertilizers in different countries

Country	Cd limit (mg/kg P)	Year limit becomes effective
Australia	345	Voluntary
Australia	300	2000
Austria	170	In effect
Belgium	200	Voluntary
Denmark	110	In effect
Finland	50	In effect
Germany	200	Voluntary
Japan	343	In effect
Norway	50	In effect
Sweden	100	In effect
Switzerland	50	In effect
Netherlands	35	Voluntary

Source: Al-Shawi and Dahl, 1999.

2.4.2 Animal Feed

Most animal diets require supplemental sources of P in addition to that present in common feedstuffs. The major types of P supplement are calcium phosphates, ammonium phosphates, sodium phosphates, and phosphoric acid (NRC, 1980). Individual feed ingredients may vary widely in composition as a result of variations in cultivation practice, growing conditions, processing and storage conditions, and nutrient status. The estimated feed efficiency and dietary mineral elements, including daily mineral requirements for growing pigs weighing between 3 and 120 kg are given in Table 2-6.

Table 2-6 : Estimated feed efficiency and dietary mineral requirements for swine.

1. Estimated feed efficiency						
Body Weight (kg)	3–5	5–10	10–20	20–50	50–80	80–120
Average weight in range (kg)	4	7.5	15	35	65	100
Estimated feed intake (g/day)	250	500	1,000	1,855	2,575	3,075
2. Mineral elements 90% dry matter (requirements % or amounts / kg of diet)						
Phosphorus, total (%)	0.70	0.65	0.60	0.50	0.45	0.40
Phosphorus, available (%)	0.55	0.40	0.32	0.23	0.19	0.15
3. Daily mineral requirements of growing pigs (requirements amount / day)						
Phosphorus, total (g)	1.75	3.25	6.00	9.28	11.59	12.30
Phosphorus, available (g)	1.38	2.00	3.20	4.27	4.89	4.61

Source: NRC, 1998.

The requirement for total P is based on a fortified, corn–soybean meal diet and takes into account the fact that some of the P in feedstuffs of plant origin is unavailable. Higher dietary concentrations of P may be required if feed intake is low (NRC, 1998). Nevertheless, feeding at a high level of P (0.8 %) resulted in a high incidence of urinary calculi (NRC, 1980). While P used as an additive in feeds is essential for animal growth, excreted manure, especially from swine and poultry production farms, poses serious problems to water quality (Syers and Cisse, 2001). Severe problems may arise when there is a high-density animal population in feedlot close to a stream, which may lead to eutrophication (Taylor and Kilmer, 1986; Sommers and Sulston, 1986) as well as accumulation of Cd and P. Though this has not yet been considered to be an issue facing the SLC, the problem is severe in Europe (Syers and Cisse, 2001).

Feedstuffs may also contain undesirable substances such as heavy metals, organochlorine compounds, chlorinated hydrocarbons, and toxins produced by parts of poisonous plants. Though toxic to animals, the presence of these substances in animal feeds cannot always be eliminated. They must not, however, exceed allowable limits. Most forages and materials fed to animals contain Cd at levels of well below 0.5 ppm on a dry weight basis, which is the maximum tolerable level of dietary Cd for livestock (NRC, 1980).