Working Paper

Mathematical Tools for Studies of Industrial Metabolism

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WP-93-9
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1. Introduction

Material flux-analysis of certain materials or chemicals (e.g heavy metals) on a regional level has become an important focus for the discussion about waste generating systems, industrial metabolism and the causes and effects of pollution and environmental quality. Material flows through society trigger the changes on local, regional and global levels. Global changes may influenceor trigger new regional developments (land use practice, population, energy development), new flows and so on.

Approaches for analysing the material fluxes of the anthroposphere (industrial society) have recently been tested [1][2].They are (generally) based on the principle that mass is neither created nor destroyed by processes, but materials may change their forms. The anthroposphere is viewed as analogous a living organism, which takes in raw materials, processes, uses and disposes of them in a degraded form that must be absorbed by the environment [3]. Since this organism is complex and poorly understood in detail, one can not count on methodological tools to provide precise assessments. The most important task seems to be the analysis of interactions between various parts of the systems, in particular the sensitivity of outflows to variations of inflows or structural changes (introduction of recycling processes, new production and waste treatment technologies, etc.). This leads to the construction of a model, which should not only analyze the present state of the considered system (region), but also include possibilities to analyze various scenarios of socio-economic, population, and energy developments and their feedback to environmental quality and the usefullness of recycling facilities.

Material flux systems include *Processes* (compartments) which are defined in terms of their characteristics to transform and transport materials [1]. In this sense waste management, water and air are considered as Processes. The Processes are connected to one another through pathways with flows, and therefore the whole system is described as a *flow-network*. The direct flows of materials between processes, such as the flow from Cd product manufacturing to air (emissions) (Fig. 1), are often relatively easy to quantify. One of the main questions is to find a method for tracing the indirect flows through the system, such as the flow from product use to Zn/Cd refining via recycling. The analysis of cycled and direct flows through the system is discussed in detail in section 3.

The goal of the industrial metabolism is improvement of pollution control and environmental quality. The current state of a material flux system can be estimated in principle by real measurements. Improvements as a result of new policy strategies such as progress towards products with low pollution content or an intended technological shift at a certain process will lead to a system perturbation. Our intuition would have difficulties in assessing the probable outcomes of such changes. Therefore models are required as an appropriate tool to optimize perturbation effects.

The analysis of material balances as well as balances of energy or impulses are essential for the understanding of various interacting processes in physics. Leontief used the idea of balances in his input- output analysis of direct and indirect requirements on interacting economic sectors to produce a unit of the final product. The importance of such an approach to the study of interacting compartments of ecological systems has been recognized only quite recently in [11]. In such studies it is assumed that the system under consideration can be partitioned into a finite number of "elements" (sectors, compartments) and a matrix of direct "flows" between them is identified. The model structure then is defined from assumptions on the flow exchanges. The model may turn out to be a set of linear or non-linear equations.

In this paper we use some results of the IIASA's Rhine Basin study [3][4] and the RAINS Model [5][12] to discuss some problems of industrial metabolism and related pollution control. These studies illustrate vast varieties of possible pollution flow structures and models.

In the analysis of the industrial metabolism as well as in economics and ecology the essential problem is to trace cycles of pollutants, products, energy etc. .Therefore it is useful to adopt the same methodology enabling to integrate metabolic processes within ecological and economic processes. This gives the opportunity to study the metabolism of various polluting systems and trace back the pollutant through various parts of the biosphere.

The approach is based on the so called transfer coefficients [1] (emission factors, production coefficients), representing the ratio of the direct flow from one process to another. The matrix of transfer coefficients (transfer matrix, production matrix) is considered as the stable part of the system, in contrast to the material flows. Such assumptions of linearity are typical for the input-output analysis.

The idea of the transfer matrix is successfully applied in the RAINS model of acidification [5] and is commonly used in pollution control models (see for example [14]). The RAINS model connects wet and dry depositions in european countries through a transfer matrix with the emissions from individual countries[1].

Together with national cost curves (energy/emissions/costs), the transfer matrix is used in an optimization procedure, for evaluating emission reduction policies as follows:

-Given an environmental target, it is necessary to determine where and how much emissions should be reduced to minimize the costs of emissions and still meet the target.

The structure of the flow-network in the RAINS model is rather simple: emissions (inflows) are directly mapped into depositions (outflows) by the transfer matrix. It allows easy assessment of the effects of emissions reductions, and can be used in the optimization procedure [12].

In the more general case of the IIASA Rhine study [3][4] there are direct and indirect patterns of flows propagating through the network, and an appropriate perturbation analysis is required to assess effects of possible modifications to the flow structure.

In this paper we describe such an analysis for discussing feasible optimization problems. The peculiarity of arising optimization problems concerns the dependency of the systems performance functions on the so-called structure matrix, which is the inverse matrix to the matrix involving the control variables. Therefore the analysis includes easily derived and existing formulas on calculations of derivatives(marginal values) of such performance

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[1]It requires three assumptions about the relations between inflows (emissions in a country) and outflows (depositions in the same or another country)

-the relationship is linear;

-the spatial distributions of emissions within a country change proportionally to changes in total national emissions;

-Considered air pollutants (SO_2,NO_x and NH_4) are not coupled by chemical interactions in the atmosphere.

functions. Such analysis is useful in the case of gradual changes and continuous optimization problems. The analysis includes also the formula on recalculation of the system indicators after discontinuous changes such as the introduction of a new technology. An example dealing with perturbation analysis is discussed in section 4, where two scenarios of a production system are examined: one without and one with recycling . The example shows that recycling increases loads on all parts of system, what may lead to negative effects unless more integrated optimization framework is considered (possibilities to reduce inflows, increase of production and waste management facilities or decrease of product use).

There may be also inherent random fluctuations of the transfer coefficients. Wind directions, precipitation, rainfalls or water levels critically affect pollutants transfer coefficients. In section 6 we outline possible approaches to deal with uncertainties in flows and in the transfer coefficients. Rarely we do find cases where all these coefficients are measured exactly, providing complete balances [6]. In general the measured values would not satisfy the principle of mass conservation, and some rules to allocate the uncertainty among the many process streams are needed. This leads to non classical constraint estimation procedures, and to rather general identification and optimization tools enabling us, in particular, to trace back sources of observable effects.

2. IIASA's Rhine Basin study and RAINS model

The IIASA's Rhine Basin study [3] includes analysis of six chemicals: cadmium (Cd), lead (Pb), zinc (Zn), nitrogen (N), phosphorus (P) and lindane. The time horizon is the period 1950 to 2010. All sources of pollution are considered.

A rich network of complex interactions within a region can be represented graphically.As an example in the present paper, we will focuss on Fig.1, which is a subsystem of the entire Cd-flow network..

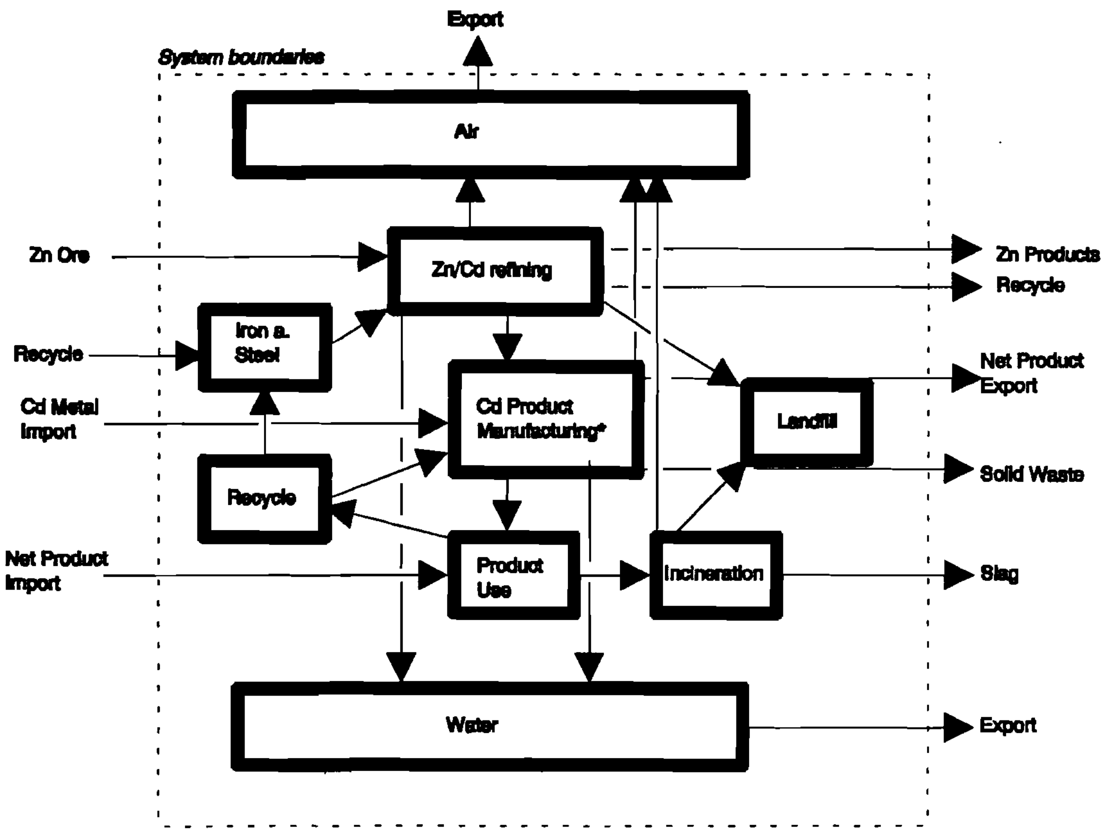

Fig. 1: Cd-production and use in the Rhine Basin[4]

The various processes (boxes, nodes) are connected directly through arrows, indicating direct material flows between them. (e.g. Cd flow directly from Refining to Cd Product Manufacturing). Since there are cycling paths in the considered system (Product Use→Recycle→Cd Product Man. ..., Product Use→Recycle→Iron and Steel→Zn/Cd Refining) there are various indirect flows (flows from one process to another via different processes) to be considered and analyzed (e.g. Refining receives flows that it generated).

It is important to consider various goods as a carriers of Cd. Since several Cd containing goods may flow into one process, one should be aware of the problem concerning the aggregation of these flows into one single flow. This could be explained with the process of Cd Product Manufacturing in Fig.1. Since this process contains the production of four different products (Battery, PVC-stablilizers, pigments, plating), using totally different production technologies, it is appropriate to consider them independently. One could then calculate an overall transfer coefficient for all the processes, but for perturbation analysis one should often consider this value as a weighted sum of four sub flows.(see section 5)

The relative importance of flows between processes can be characterized by transfer coefficients estimated by various means. As an example of transfer coefficient estimation based on literature data, we use the process of Pigment Manufacturing (Fig. 2), which is a subprocess of Cd product manufacturing.

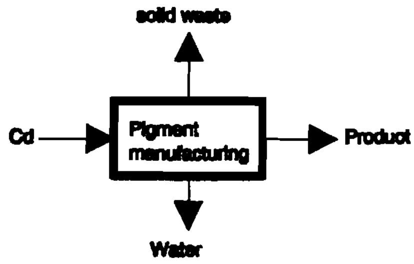

Fig. 2

The procedure for estimating the transfer coefficients of this process is provided in [4] to calculate aqueous cadmium emissions for the year 1984. It is reported that during pigment production, the following partitioning of cadmium takes place:

-94 % goes to product ,
-6 % is lost in production of which:
 4.47% is reclaimed in the plant,
 1.4% is emitted to municipal treatment plants and
 0.12 % is directly charged to water

With an efficiency of A% of the sewage treatment plant, the % E of discharged cadmium would be

$$1.4*A+0.12=E\%$$

For the river-Rhine basin this leads to the following aqueous transfer coefficients[2] for the year 1984:

0.0082.................................with waste water treatment efficiency 50 %
0.0026.................................with waste water treatment efficiency 90 %
0.0012.................................with waste water treatment efficiency 100 %

---

[2]These transfer coefficients have been calculated in [4] by a combination of various sources:

-1 direct measurement of emissions
-2 literature data on emissions
-3 literature data on transfer coefficients (emission factors)
-4 legislation on maximum allowed emissions

The flows obey the principle of mass conservation (water treatment leads to aqueous and solid wastes). Therefore the transfer cofficients of a process sum up to 1.0, and their rigorous estimation can be achieved only by using such constraints and optimization techniques.

The use of transfer coefficients is a central idea of IIASA's RAINS model [5]. The process of acidification from sources to receptors can be interpreted as a flow network of the following simplest structure (Fig. 3).

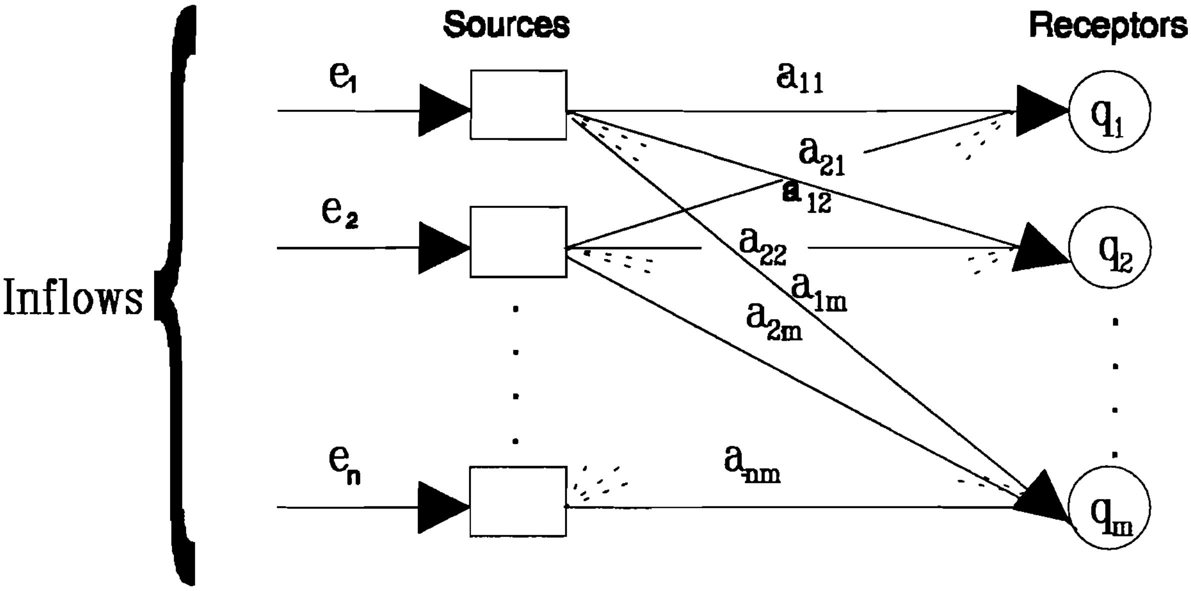

Fig. 3: The structure of the flow network of the RAINS model

Here a_{ij} is defined as the transfer coefficient of deposition at receptor j per unit of emission from source (country) i. The transfer matrix $A=\{a_{ij}\}$ maps directly inflows (emissions) $e=(e_1,...,e_n)$ into outflows (depositions) to the environment (receptors). The deposition d_j at any location j is computed by

$$d_j = \sum_{i=1}^{n} e_i a_{ij}, \qquad j=1,...,m \tag{1}$$

Such a simple source-receptor relationship permits the analysis and development of various emission reduction policies in order to optimize total reduction costs

$$\sum_{i=1}^{n} \varphi_i(e_i)$$

subject to constraints on critical loads (depositions) defined by levels q_j:

$$\sum_{i=1}^{n} e_i a_{ij} \le q_j, \qquad j=1,...,m$$

where $\varphi_i(e)$ is an emission reduction cost at source i. Similar optimization problems for general flow networks are described in section 5.

The transfer coefficients a_{ij} in the previous equations are derived from calculations of the EMEP model of the Norwegian Meterological Institute. Changes or errors in these coefficients affect depositions (outflows) linearly due to the simple structure of the RAINS model (see Fig.3).

The Rhine Basin model has a more complicated structure (direct and indirect flows) and one should be aware of the non linear relations between flows and transfer coefficients due to cycling, which could change the whole characteristic of the system.

Let us now discuss it in more detail.

3.The mass balance approach

Various waste generating systems can be interpreted as material flow systems. Processes are selected with the identification of their input and output flows. Within each process the transfer of mass is accounted for, so that the time rate of change of mass (flows) is expressed as input of materials minus output. An overall balance for each process may be written as:

$$\dot{x}_i^l = \frac{dx_i^l}{dt} = \sum_{j=0}^{n} F_{ji}^l - \sum_{j=0}^{n} F_{ij}^l \pm f_i^l(x), \quad i=1,...,n. \tag{2}$$

where x_i^l is the mass of material l within process i., $f_i^l(x)$ accounts for transformations of material l into other materials and n is the number of processes in the system (region). In the following we focus on systems with one material and no transformations (f(x)=0).The possible flow of materials from process i to j is indicated by F_{ij} . F_{i0} and F_{0i}, representing interactions with the "environment" (processes outside of the system boundaries).The flows F_{0i} are regarded as inputs which drive the system. Useful insights into interconnections between processes (compartments) are derived from the assumption

$$\dot{x}_i \equiv 0, \qquad i=1,...,n \tag{3}$$

which corresponds to the static, steady state analysis. This assumption is important in a study of interconnections between various parts of the system.

Next we assume that the F_{ij} can be expressed as a fraction of the so called throughflows χ_i of the donor compartment i (throughflow is defined as the total input of mass into compartment i within a considered time unit)

$$F_{ij} = a_{ij}\chi_i, \qquad i=1,...,n, j=0,...,n \tag{4}$$

In this case process i is characterized by the vector $a_i=(a_{i0},...,a_{in})$, where a_{ij} can often be considered as a constant coefficient independent of χ_i. Since each output to compartment i is represented by a portion of throughflow χ_i, it follows with (2) and (3)

$$\sum_{j=0}^{n} a_{ij} = 1, \quad a_{ij} \geq 0. \tag{5}$$

for all i=1,...,n and j=0,...,n.

Thus equation (2) becomes :

$$\chi_j = \sum_{i=1}^{n} a_{ij}\chi_i + F_{0j}, \qquad j=1,..,n. \tag{6}$$

where F_{oi}, j=1,...,n, are the driving inflows. Equation (6) defines similarly to the well-known Leontief input-output model, one tool to analyze material flows of an economic system.

In many cases the linear hypothesis (4) is not sufficiently well justified. Several nonlinear models exist. The following example presents one kind of non-linearity:

$$F_{ij} = a_{ij}\chi_i\chi_j,$$

which is used in studies of population dynamics.

The total inflow to the system is

$$\sum_{i=1}^{n} F_{0i},$$

and the total outflow

$$\sum_{i=1}^{n} F_{i0}.$$

All processes are mutually dependent via interconnected causal chains with overlaps and feedback. In addition to direct dependencies, systems variables are also indirectly influenced by propagation along several dependency sequences. It is possible to speak of a direct flow path and a sequential flow path. Because of equation (4) the direct flow from process i to process j is expressed as a fraction of the throughflow χ_i. Flow input-output analysis techniques allow accounting also of direct and indirect sequential flows to find the total input χ_i to i.

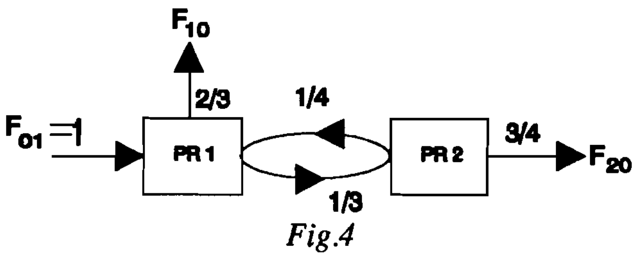

Fig.4

In order to illustrate the problem, let us consider a system with two processes, PR1 and PR2 (Fig.4), F_{oi}=1 and the transfer coefficients are shown at the arrows. The direct flow from Process 1 to the environment is 2/3. The indirect flow is due to the cycle between process 1 and process 2, and is calculated with the following infinite series:

$$(1/3\cdot 1/4).\frac{2}{3}+(1/3\cdot 1/4)^2.\frac{2}{3}+(1/3\cdot 1/4)^3.\frac{2}{3}+...=\frac{2}{3}\sum_{k=1}^{\infty}(1/12)^k$$

The notion of so-called structure matrix allows such calculations for tracing various dependencies of general networks. In matrix form Eq. (6) can be compactly written as

$$\chi=\chi A+F=F(\mathrm{I}-A)^{-1} \tag{7}$$

where $\chi=(\chi_1,...\chi_n)$, $y=(F_{01},...,F_{0n})$ are row vectors, $A=(a_{ij},\ i,j=1,...,n)$ is a nxn matix and I is the identity matrix.

Equation (7) can be written as

$$\chi_j=F_{01}(1-A)^{-1}_{1j}+...+F_{0i}(1-A)^{-1}_{ij}+...+F_{0n}(1-A)^{-1}_{nj} \tag{8}$$

where elements

$$(I-A)^{-1}_{ij}$$

of the matrix $(I\text{-}A)^{-1}$ specify fractions of throughflow at j, caused by inflow F_{0i} at i.

The value

$$(I-A)^{-1}_{ij}F_{oi}$$

represents flow at j sequentially propagated over all paths of all lengths from i in response to input F_{0i}.Therefore the inverse matrix $(1\text{-}A)^{-1}$ accounts for all dependency paths and is called the structure matrix.The equality

$$(I-A)^{-1}_{ii}=1$$

implies that process i receives only inflow that it did not generate. If

$$(I-A)^{-1}_{ii}>1\ ,$$

then the difference

$$(I-A)^{-1}_{ii}-1>0$$

represents flows once generated by i and returned to i by loops.

Therefore, loop return flows are a component of the total contribution of i to the intrasystem cycling. They may be computed directly as (see [7])

$$[(I-A)^{-1}_{ii}-1]F_{0i}$$

4. Production-waste management system. Simulation procedure.

Consider a rather typical situation which illustrates introduced notations and techniques. The environmental quality of a region is affected as it is shown in Fig. 5 by interactions between production, product use , and waste management processes.

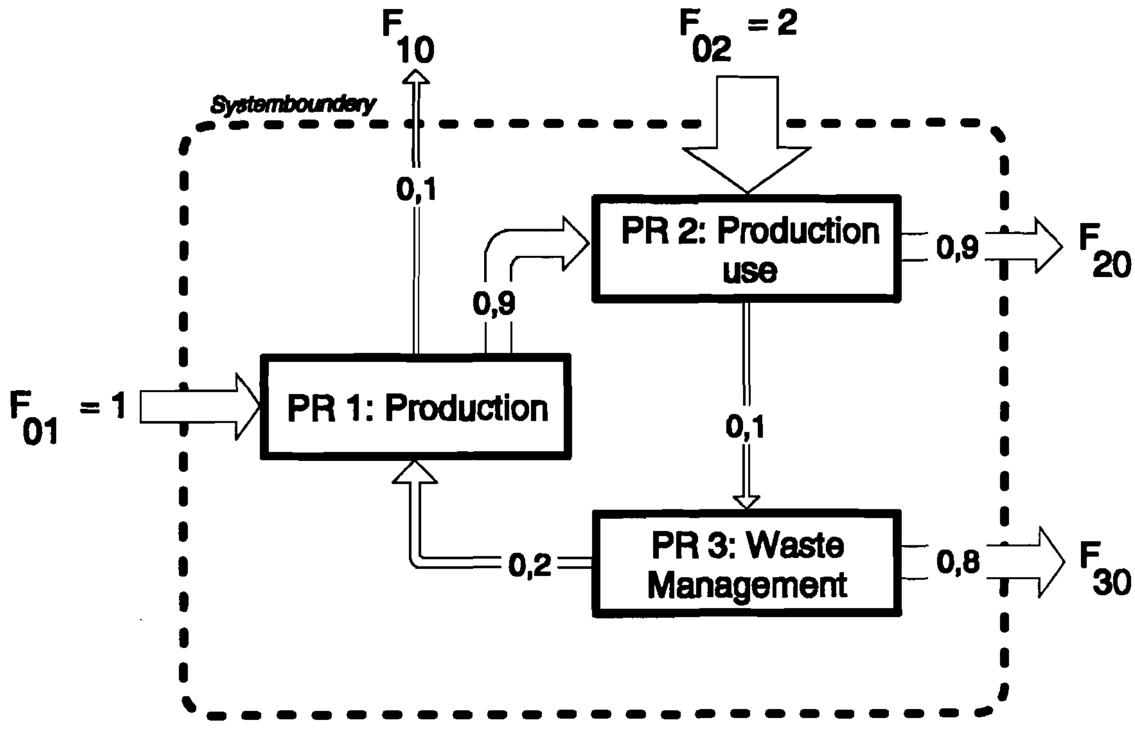

Fig.5 (system without recycling)

Process 1 (PR1) is considered to be an industrial production process with "pollutant inflow" of raw material (import) F_{01}=1. Process 2 is considered as product use, with a certain amount of "polluted" import F_{02}=2. The third process is a waste management facility, which recovers a certain amount of raw material (flow into production) with the transfer coefficient a_{31}=0,2. The transfer cofficients are fixed quantities and form the matrix A:

from/to	PR1	PR2	PR3
PR1	0	0,9	0
PR2	0	0	0,1
PR3	0,2	0	0

The existence of a return flow from PR2 to PR3 and then to PR1, results in a flow through PR1 greater then the inflow F_{01}=1. Value of flows through all processes 1,2 and 3 can be established by real measurements. In fact the knowledge of the transfer coefficients matrix allows the calculation of the throughflows automatically , by calculating the structure matrix $(I-A)^{-1}$ (see Equ. (7),(8)).

Let us notice that the throughflows for processes 1.2 and 3 satisfy the balance equations (6) :

$$\chi_1 = 0,2\chi_3 + 1 \qquad (total\ \ inflow\ \ into\ \ PR1)$$

$$\chi_2 = 0,9\chi_1 + 2 \qquad (total\ \ inflow\ \ into\ \ PR2)$$

$$\chi_3 = 0,1\chi_2 \qquad (total\ \ inflow\ \ into\ \ PR3)$$

The matrices

$$A = \begin{pmatrix} 0 & 0,9 & 0 \\ 0 & 0 & 0,1 \\ 0,2 & 0 & 0,7 \end{pmatrix}, 1 - A = \begin{pmatrix} 1 & -0,9 & 0 \\ -0,8 & 1 & -0,1 \\ -0,2 & 0 & 1 \end{pmatrix}$$

and the structure matrix

$$(1 - A)^{-1} = \begin{pmatrix} 1,02 & 0,92 & 0,09 \\ 0,02 & 1,02 & 0,1 \\ 0,2 & 0,18 & 1,02 \end{pmatrix}.$$

Since the vector of inflows (F_{01}, F_{02}, F_{03})=(1,2,0), then the values of throughflows satisfying the above mentioned balance equations are calculated by formula (8):

$$\begin{aligned} \chi_1 &= 1 \cdot 1,02 + 2 \cdot 0.02 = 1,06 \\ \chi_2 &= 1 \cdot 0,92 + 2 \cdot 1,02 = 2,95 \\ \chi_3 &= 1 \cdot 0,09 + 2 \cdot 0,1 = 0,3 \end{aligned}$$

The propagation of inflows F_{01}=1, F_{02} =2 through the system can be seen from the following process, simulating the dynamic of flows in the system.
At the initial step s=0 the throughflows are simply equal to the inflows :

$$\chi_1^0=1,\ \chi_2^0=2,\ \chi_3^0=0$$

For the next steps s=1, 2, ... we have according to the balance equations:

$$\begin{aligned} s = 1\ \ \chi_1^1 &= 0,2\chi_3^0 + 1 = 1 \\ \chi_2^1 &= 0,9\chi_1^0 + 2 = 2,9 \\ \chi_3^1 &= 0,1\chi_2^0 + 0,7\chi_3^0 = 0,29 \end{aligned}$$

$$\begin{aligned} s = 2\ \ \chi_1^2 &= 0,2\chi_3^1 + 1 = 1,04 \\ \chi_2^2 &= 0,9\chi_1^1 + 2 = 2,9 \\ \chi_3^2 &= 0,1\chi_2^1 = 0,29 \end{aligned}$$

$$\begin{aligned} s = 3\ \ \chi_1^3 &= 0,2\chi_3^2 + 1 = 1,058 \\ \chi_2^3 &= 0,9\chi_1^2 + 2 = 2,936 \\ \chi_3^3 &= 0,1\chi_2^2 + 0,7\chi_3^2 = 0,29 \end{aligned}$$

If we proceed further in the same manner, the throughflows will settle down at the levels

$$\chi_1=1{,}06,\ \chi_2=2{,}95,\ \chi_3=0{,}3$$

Such a simulation process can be also used as a solution procedure for the balance equations(6). The diagonal elements of the matrix $(I-A)^{-1}$ (each of them is equal to the fractions of throughflow to a process caused by inflow to the same process) are greater then one. This is a result of the indirect flow structure of the system. Due to this structure, import flows cycle through the system, and may contribute several times to the throughflow of each process, which is clear from the described simulation procedure.
The throughflow for PR1 is equal to 1,06 and it reflects flows propagated over all possible paths of all possible length to PR1 in response to the inflows. It can also be interpreted as the raw material demand of PR1. The element $(I-A)^{-1}_{11}=1{,}02$ of the structure matrix shows that the loop return flow for PR1 is equal to

$$(1{,}02-1)\cdot 1=0{,}02$$

The throughflow χ_3 is 0,3, which is the amount of pollutant needed to be managed in PR3. Any change in the structure of the system, for instance an increase of the transfer coefficient a_{31} for recycling, or a decrease of the transfer coefficients may essentially affect the throughflow χ_3 and thus lead to higher or lower requirements (e.g technical changes) on the waste treatment facilitiy.
For example, suppose a possible scenario of future developments in the region includes an efficient recycling facility from PR2 to PR1 with the transfercoefficient $a_{21}=0{,}8$ (Fig.6). Clearly such a study is impossible without a model. Otherwise it requires real-life "trial and error" experiments . A straightforward approach can be based on recalculating the inverse matrix $(I-A)^{-1}$, which is a time consuming task. In the next section we describe tools for quick assessment of structural changes without recalculating $(I-A)^{-1}$.Such tools can be efficiently incorporated in various policy oriented studies.

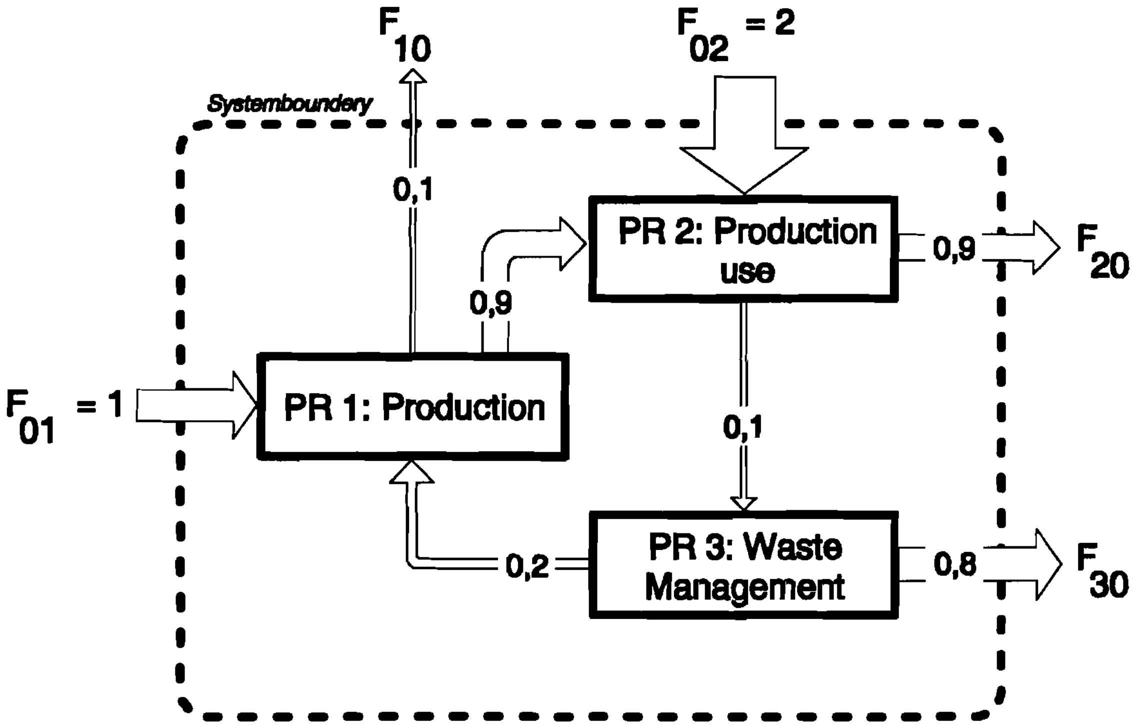

Fig.6 (system with recycling)

Simply by recalculating $(I-A)^{-1}$ we can compute possible future throughflows:

$$\chi_1=10{,}08\ \chi_2=11{,}07,\ \chi_3=1{,}11$$

If we compare this values with these calculated for Fig. 5 we see that all throughflows are much higher. This means that in this scenario we have more production, which needs a higher product use (product demand) and leads to more waste. The economic structure and the enviromental impacts are totally changed. Nevertheless the scenario shows that there is a possibility to save raw material by introducing recycling from PR1 to PR2.
If we do such kind of analysis the next question are wether the changes are benificial, and what are the corresponding costs and benefits.
There may be other possibilies to reduce pollution (i.e taxes on throughflows) what again can be studied by recalculating throughflows and associated costs and benefits. Next section will deal with the search techniques for optimal improvements.

5. Perturbation and Sensitivity Analysis, Agregation Optimization

One of the main reasons for building a model is to compare possible management strategies affecting inflows, parameters and/or the structure of the system. Which part of the system is most sensitive to changes ? Which direction of changes should be accepted? What are effects of changes ? These are typical questions to be examined by perturbation analysis.

Firstly, from Eq. (8) the effects (sensitivity) on throughflows caused by small changes of inflows are established as

$$\frac{\partial \chi_i}{\partial F_{0j}} = (I-A)^{-1}_{ji} \tag{9}$$

Thus the sensitivity of throughflow χ_1, in our example introduced in chapter 4, to the change of inflow F_{01} and F_{02} is calculated respectively as 3,82 and 3,13. Since throughflow to the enviroment $F_{10}=0{,}1\chi_1$, the sensitivity of this variable to a change in the inflows is assessed as $0{,}1 \cdot 3{,}82 = 0{,}382$ and $0{,}1 \cdot 3{,}13 = 0{,}313$.

This means that a decrease of one unit of "imported pollution" F_{02}, will lower the pollution at the process 1 by 0,313 .

Large changes in inflows from F_{oi} to $\overline{F_{oi}}$ modify the throughflows as

$$\overline{\chi_i} = (I-A)^{-1}_{1i}\overline{F_{01}} + (I-A)^{-1}_{2i}\overline{F_{02}} + \ldots + (I-A)^{-1}_{ni}\overline{F_{0n}}$$

Therefore the structure matrix $(I-A)^{-1}$ allows fast assessment of the effects of inflow changes, particulary fast calculation of throughflows and deposition to the "environment" (processes out of system boundaries), even as functions of time t:

$$\chi_i^t = (I-A)^{-1}_{1i}F_{01}^t + (I-A)^{-1}_{2i}F_{02}^t + \ldots + (I-A)^{-1}_{ni}F_{0n}^t,\quad F_{i0}^t = a_{i0}\chi_i^t\ , \tag{10}$$

where χ_i^t is the throughflow at i caused by the inflows $F_t=(F_{01}^t,...,F_{0n}^t)$ at time t. Thus in the case of general material flow networks the matrix $(I-A)^{-1}$ reduces the study of pollution (throughflows through certain processes like air and water) in time to the simplest case of the RAINS type model described by equation (1).

Changes of inflows trigger a dynamic of the system. Of course, there may also be slow changes of parameters a_{ij} (transfer matrix) in time or large changes in this coefficient due to faults or other structural changes (technological improvements, new treatment or production facilities etc.). For example new recycling technologies can be interpreted as the change of a transfer coefficient a_{ij} from 0 to a positive value.

For the investigation of pollution and possible changes, it is important to know how changes in the transfer coefficients alter the throughflows χ_i. .

Suppose the matrix A in (7) is changed to $A+\delta A$. This change alters χ to $\chi+\delta\chi$ and can be calculated in general by the following equation:

$$\begin{aligned} &\chi+\delta\chi=(A+\delta A)(\chi+\delta\chi)+F \\ &\Leftrightarrow \delta\chi=\delta\chi(A+\delta A)+\chi\delta A \end{aligned} \tag{11}$$

Suppose the structure matrix $(I-A)^{-1}$ is known, and all coefficients of δA are zero except $\delta_{i1}, ..., \delta_{in}$:

$$\delta A=\delta_i A=\begin{pmatrix} 0 & 0 & \dots & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \delta_{i1} & \delta_{i2} & \dots & \dots & \delta_{in} \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \dots & 0 \end{pmatrix}=\begin{pmatrix} 0 \\ \dots \\ 1 \\ \dots \\ 0 \end{pmatrix}\langle \delta_{i1} \quad \delta_{i2} \quad \dots \quad \dots \quad \delta_{in}\rangle$$

This case corresponds to changes only in one process (compartment).

The matrix $(I-A-\delta A_i)^{-1}$ can be calculated through simple adjustments of $(I-A)^{-1}$. It is easy to see that for any row and column vectors

$$\alpha=\langle\alpha_1,\dots,\alpha_n\rangle,\ \beta^T=\begin{pmatrix}\beta_1\\ \dots \\ \beta_n\end{pmatrix}$$

the following identity holds

$$(I-A-\beta^T\alpha)^{-1}=(I-A)^{-1}+(1-\alpha(I-A)^{-1}\beta^T)^{-1}(I-A)^{-1}\beta^T\alpha(I-A)^{-1}$$

This identity is verified by multiplying both sides by $(I-A-\beta^T\alpha)$. Since $\alpha(I-A)^{-1}\beta^T$ is a number, then

$$\begin{aligned} &(I-A-\beta^T\alpha)^{-1}(I-A-\beta^T\alpha)=I+(1-\alpha(I-A)^{-1}\beta^T)^{-1}(I-A)^{-1}\beta^T\alpha- \\ &(I-A)^{-1}\beta^T\alpha-(1-\alpha(I-A)^{-1}\beta^T)^{-1}(I-A)^{-1}\beta^T\alpha(I-A)^{-1}\beta^T\alpha= \end{aligned}$$

$$= I + (1-\alpha(I-A)^{-1}\beta^T)^{-1}(I-A)^{-1}\beta^T\alpha - (I-A)^{-1}\beta^T\alpha -$$
$$-\alpha(I-A)^{-1}\beta^T(1-\alpha(I-A)^{-1}\beta^T)^{-1}(I-A)^{-1}\beta^T\alpha =$$
$$= (I + (1-\alpha(I-A)^{-1}\beta^T)^{-1}(I-A)^{-1}\beta^T\alpha[1-\alpha(I-A)^{-1}\beta^T] -$$
$$-(I-A)^{-1}\beta^T\alpha = I + (I-A)^{-1}\beta^T\alpha - (I-A)^{-1}\beta^T\alpha = I$$

If $\beta^T\alpha$ corresponds to the matrix $\delta_i A$ then

$$\alpha = \langle \delta_{i1}, \ldots, \delta_{in} \rangle, \quad and \quad \beta^T = \left\langle \begin{matrix} \bar{0} \\ 1 \\ \bar{0} \end{matrix} \right\rangle,$$

$$\alpha(I-A)^{-1}\beta^T = \sum_{k=1}^{n} \delta_{ik}(I-A)^{-1}_{ki}$$

and

$$(I-A-\delta_i A)^{-1} = (I-A)^{-1} + [1-\sum_{k=1}^{n}\delta_{ik}(I-A)^{-1}_{ki}]^{-1}(I-A)^{-1}\delta_i A(I-A)^{-1} \qquad (12)$$

It allows calculation of $\delta\chi$ from Eq. (11) without the inversion of the new transfer matrix $(I-A-\delta_i A)^{-1}$.

Suppose now the coefficients of the matrix A depend on some parameters $u=(u_1,\ldots,u_l)$, . In particular u may be determined from the transfer coefficients $u=\{a_{ij}\}$. Situations when coefficients a_{ij} are affected by some parameters appear in various input output models (e.g overall dependencies of water quality models on temperature, meteorological parameters, chemical and physical process dependencies on thermodynamic parameters). This may also be the case when a certain process i is composed of a number of subprocesses $k=1,\ldots,R_i$ and the coefficients a_{ij} are in fact the aggregation of transfer coefficients u_{ij}^k of all subprocesses $k=1,\ldots,R_i$:

$$a_{ij} = \sum_{j=1}^{R_i} v_{ij}^k u_{ij}^k, \quad \sum_j u_{ij}^k = 1, \quad u_{ij}^k \geq 0,$$

with weights v_{ij}^k fullfilling the normalization:

$$\sum_k v_{ij}^k = 1$$

Then a change can be achieved by changes in values of transfercoefficients u_{ij}^k subject to the normalization conditions.

From the identity

$$0 = \frac{\partial I}{\partial u_k} = \frac{\partial (I-A)(I-A)^{-1}}{\partial u_k} = -\frac{\partial A}{\partial u_k}(I-A)^{-1} + (I-A)\frac{\partial (I-A)^{-1}}{\partial u_k}$$

it follows that

$$\frac{\partial (I-A)^{-1}}{\partial u_k} = (I-A)^{-1}\frac{\partial A}{\partial u_k}(I-A)^{-1} \qquad (13)$$

If the vector u includes only entries of A and $u_k=a_{ij}$, then

$$\frac{\partial A}{\partial a_{ij}} = \begin{array}{c@{}c} \begin{array}{ccccc} & & j & & \\ \end{array} & \\ \left\langle \begin{array}{ccccc} 0 & \dots & 0 & \dots & 0 \\ 0 & \dots & 1 & \dots & 0 \\ 0 & \dots & 0 & \dots & 0 \\ 0 & \dots & 0 & \dots & 0 \end{array} \right\rangle & \begin{array}{c} \\ i \\ \\ \\ \end{array} \end{array}$$

and

$$\frac{\partial (I-A)^{-1}_{kl}}{\partial a_{ij}} = (I-A)^{-1}_{ki}(I-A)_{jl}^{-1} \tag{14}$$

By using this formula we can study the sensitivity of throughflow χ_3 of the waste treatment process 3 in Fig. 6 to changes in the transfercoefficients a_{21}, a_{23}.
Since (see formula 8)

$$\chi_3 = 1 \cdot (I-A)^{-1}_{13} + (I-A)^{-1}_{23}$$

then the sensitivity of χ_3 is assessed through the sensitivity of $(I-A)^{-1}_{13}$ and $(I-A)^{-1}_{23}$.
We have

$$\frac{\partial (I-A)^{-1}_{13}}{\partial a_{21}} = (I-A)^{-1}_{12}(I-A)^{-1}_{13} = 1{,}18$$

$$\frac{\partial (I-A)^{-1}_{13}}{\partial a_{23}} = (I-A)^{-1}_{12}(I-A)^{-1}_{33} = 4{,}097$$

$$\frac{\partial (I-A)^{-1}_{23}}{\partial a_{21}} = (I-A)^{-1}_{22}(I-A)^{-1}_{13} = 1{,}311$$

$$\frac{\partial (I-A)^{-1}_{23}}{\partial a_{22}} = (I-A)^{-1}_{22}(I-A)^{-1}_{33} = 4{,}079$$

Therefore

$$\frac{\partial \chi_3}{\partial a_{21}} = \frac{\partial (I-A)^{-1}_{13}}{\partial a_{21}} + 2 \cdot \frac{\partial (I-A)^{-1}_{23}}{\partial a_{21}} = 1{,}18 + 2 \cdot 1{,}311 = 3{,}8$$

$$\frac{\partial \chi_3}{\partial a_{23}} = \frac{\partial (I-A)^{-1}_{13}}{\partial a_{23}} + 2 \cdot \frac{\partial (I-A)^{-1}_{23}}{\partial a_{23}} = 4{,}079 + 2 \cdot 4{,}079 = 12{,}2$$

Thus the change of waste flows from PR2 to PR3 affects the waste treatment facility three times greater than the change of the recycling flow from PR1 to PR2.
The complete increment of $(I-A)^{-1}$ from changes in the parameters $u=(u_1,\dots,u_l)$

$$d(I-A)^{-1} = \sum_{k=1}^{l} \frac{\partial (I-A)^{-1}}{\partial u_k} du_k \tag{15}$$

One can also reverse the analysis and assess the changes in A by modifying $(I-A)^{-1}$, which can be interpreted by asking how to modify the direct flow structure to generate a particular subsequential structure.

The sensitivity of throughflows $\chi=(\chi_1,...,\chi_n)$ can be assessed by derivatives

$$\frac{\partial \chi_i}{\partial u_k}, \qquad i=1,...,n\ ,k=1,...,n,$$

Such analysis can also be interpreted as the assessed effects of changes in the direct flows on the sequential flows (indirect flows) . By Eq. (6) this is equivalent to the question of how do small changes in the elements of A affect $(I-A)^{-1}$.

The techniques described above allow for various optimization approaches. Equation (7) or

$$\chi_i = \sum_{k=1}^{n} (I-A)^{-1}_{ki} F_{0k} \tag{16}$$

and relations

$$F_{i0} = a_{i0}\chi_i$$

map inflows into throughflows and outflows.
This relation can be applied similarly to the RAINS model to accomplish the task: Given an environmental target it is necessary to determine where and how much inflow should be modified to minimize associated costs.

The simplest optimization problem analogous to the RAINS model (see section 2) corresponds to the minimization of a total cost function

$$\sum_{k=1}^{n} \varphi_k(F_{ok}) \tag{17}$$

subject to a certain target at receptors $j \in J$

$$\sum_{k=1}^{n} (I-A)^{-1}_{kj} F_{0k} \le q_l, \quad j \in J \tag{18}$$

where J is the set of processes-receptors such as air and water in Fig.1.

Control variables of the RAINS model and the model (17)-(18) are only levels of emissions (inflows) F_{0k}, k=1,...,n. In the general case of the Rhine study and other waste generating systems, material flows can also be controlled by changing of the transfer matrix

$$A = (A_1, A_2, ..., A_n), \quad A_k = \left\langle \begin{matrix} a_{1k} \\ a_{2k} \\ \cdots \\ a_{nk} \end{matrix} \right\rangle, \quad A_0 = \left\langle \begin{matrix} a_{10} \\ a_{20} \\ \cdots \\ a_{n0} \end{matrix} \right\rangle,$$

Let a function $f(\chi,A,A_0,F)$ characterize effects of changes (costs, benefits or other indicators). We assume f is a continuously differentiable function. Then the change of A, A_0 and F to $A+\delta A$, $A_0+\delta A_0$, and $F+\delta F$ results in an incremental increase or decrease of function $f(\chi,A,A_0,F)$ by

$$\delta f = (f_\chi, \delta\chi) + (f_A, \delta A) + (f_{A_0}, \delta A_0) + (f_F, \delta F) + O(\|\delta A\| + \|\delta A_0\| + \|\delta F\|) \tag{19}$$

where $f_\chi = (\frac{\partial f}{\partial \chi_1},...,\frac{\partial f}{\partial \chi_n})$, $f_F = (\frac{\partial f}{\partial F_{01}},...,\frac{\partial f}{\partial F_{0n}})$, $f_{A_0} = (\frac{\partial f}{\partial a_{1o}},...,\frac{\partial f}{\partial a_{n0}})$ and f_A is represented as the matrix

$$f_A = \begin{pmatrix} \frac{\partial f}{\partial a_{11}} & \cdots & \frac{\partial f}{\partial a_{1n}} \\ \cdots & \cdots & \cdots \\ \frac{\partial f}{\partial a_{n1}} & & \frac{\partial f}{\partial a_{nn}} \end{pmatrix} = (\frac{\partial f}{\partial A_1},...,\frac{\partial f}{\partial A_n})^T.$$

The first three terms on the right hand side of Eq.(19) are defined as

$$(f_\chi, \partial\chi) = \sum_{i=1}^{n} f_{\chi_i} \delta\chi_i,$$

$$(f_F, \partial F) = \sum_{i=1}^{n} f_{F_{oi}} \delta F_{0i},$$

$$(f_{A_0}, \partial A_0) = \sum_{i=1}^{n} f_{a_{i0}} \delta a_{i0}$$

$$(f_A, \partial A) = \sum_{i=1}^{n} (\frac{\partial f}{\partial A_i})^T \delta A_i,$$

where f_y is the partial derivative of f with respect to y.

According to Eq. (16) the vector of throughflows depends on A and F. Therefore the increment $\delta\chi$ can be expressed through δA and δF.

$$\delta\chi = \sum_{l=1}^{n} (\frac{\partial \chi_l}{\partial A}, \delta A_l) + (\frac{\partial \chi}{\partial F}, \delta F) + O(\|\delta A\| + \|\delta F\|)$$

where

$$\frac{\partial \chi}{\partial A} = (\frac{\partial \chi_1}{\partial A},...,\frac{\partial \chi_n}{\partial A}),\ \frac{\partial \chi}{\partial F} = (\frac{\partial \chi_1}{\partial F},...,\frac{\partial \chi_n}{\partial F})$$

These derivatives are calculated by Eqs. (9) and (13).

Negative or positive values δf indicate the direction of improvements. The Eq. (11) and (12) can be used in assessing alternative technologies for a process i characterized by transfer coefficients

$$(a_{i1},...,a_{in}) \text{ and } (\bar{a}_{i1},...,\bar{a}_{in}) = (a_{i1}+\delta a_{i1},...,a_{in}+\delta a_{i1}).$$

The Eqs. (8),(10),(11),(12),(13) permit the solving of various optimization problems taking into account possible constraints such as the normalization constraint Eq.(5) or the enviromental constraints of Eq.(18).

6. Uncertainties, Identification, Time-varying flows and Stochastic Optimization

The basic element in the analysis of material flows is the input -output modelling of a single process, which is defined through its characteristic to transfer material flows. The above described analysis is based on the assumption that the transfer coefficients a_{ij} of Eq. (6) are deterministic . Rarely we do find practical problems where all the inputs and outputs have been measured directly without errors. Most flows are only known within a range. Even in the simplest processes we face uncertainties caused by different sources (measurements, material-content of goods etc.). In many cases it is natural to treat the transfer coefficients as stochastic variables rather then deterministic one. For example, in the RAINS model the transfer coefficients are affected by uncertainties in lifetimes of pollutants , mechanism of pollutant's generation and weather conditions .

Let us discuss two typical situations on calculations of mass balances involving uncertainties. In the first situation uncertainties arise from measurements, whereas the second concerns uncertainties inherently in the pollution flows.

Consider as in [6] a separation process (Fig.7)

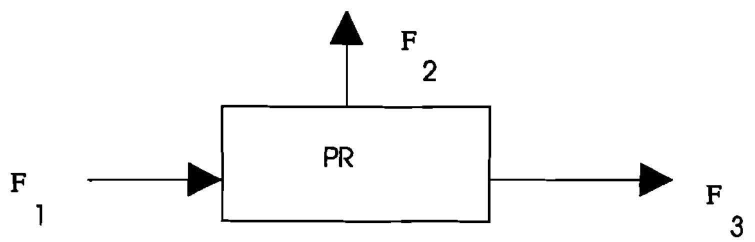

Fig.6 Separation Process

with inflow F_1 and outflows F_2, F_3.For example F_2 is the magnitude of air pollution and F_3 are captured pollutants. Deterministic flows fulfil the balance equations

$$F_1 = F_2 + F_3$$

It is also possible to define the process capture fraction α such that $F_2 = \alpha \cdot F_1$, $F_3 = (1-\alpha) \cdot F_1$ or $F_2 = a_1 \cdot F_1$, $a_1 + a_2 = 1$, $a_1 \geq 0$, $a_2 \geq 0$, where a_1 and a_2 are the tranfer coefficients($a_1=\alpha$, $a_2=1-\alpha$ in this case).

In practice flows F_1, F_2 and F_3 are measured or metered only with errors, providing flow readings as (usually) independent random variables δ_1, δ_2, and δ_3. Clearly, that

$$\delta_1 \neq \delta_2 + \delta_3$$

which leads to the problem of finding flow estimates $\hat{F}_1, \hat{F}_2, \hat{F}_3$ satisfying the balance equations and minimizing a certain measure of errors. For example, minimizing the expected square of error function (risk function)

$$R(F) = E(\delta_1 - F_1)^2 + E(\delta_2 - F_2)^2 + E(\delta_3 - F_3)^2$$

subject to the balance equation, where E is the mathematical expectation symbol.

In a more general case direct flows F_{ij} between a process i and a process j, i,j=1,...,n, fulfil the following equation

$$\sum_{j=0}^{n} F_{ij} - \sum_{j=0}^{n} F_{ji} = 0, \qquad i=1,....,n$$

If δ_{ij} are (dependent or independent) flow readings, then the estimation of true values F_{ij} is equivalent to the stochastic optimization problem: find values $\hat{F}_{ij}$ minimizing the expected risk function

$$R(F) = \sum_{i,j} E(\delta_{ij} - F_{ij})^2$$

subject to the above balance equations. When uncertainties in the measured flows δ_{ij} are different for each flow, we can take into account a certain weight Y_{ij} in the risk function.. The risk function to be minimized can be written as

$$R(F) = \sum_{i,j} Y_{ij} E(\delta_{ij} - F_{ij})^2$$

There are simple implemented procedures to solve such an estimation problem and even more general problems with more general risk functions

$$R(F) = \sum_{i,j} E\varphi_{ij}(\delta_{ij}, F_{ij}),$$

where φ_{ij} characterize a "fitness" measure.

So far we assumed that the true flows F_{ij} are deterministic. In many practical situations these flows are inherently stochastic , affected by several parameters, like "technological" characteristics, weather conditions or accidents. It might be useful if one represents randomness in flows through the randomness of the transfer coefficients. Therefore we assume that

$$F_{ij} = a_{ij}\chi_i$$

where a_{ij} are random transfer coefficients and χ_i is the throughflow of process i. It leads to balance equations (6) as equations with random coefficients and random inflows.

It is always possible to think of random parameters a_{ij} and F_{0i} as variables $a_{ij}(\omega)$, $F_{0i}(\omega)$ defined on a set Ω of events ω equipped with a probability measure $P(d\omega)$ with a set $\mathcal{A}$ of P-measurable events (the probability of such an event is defined). A special case is the case of time varying flows. It could be also fruitful to define transfer coefficients as random variables, since flows are affected by seasonable fluctuations of various parameters like temperature , leakages etc. . In such cases the distribution of ω is defined by frequencies of possible variations in the transfer coefficients during the given time interval. Therefore the fluctuations $\chi(\omega)=(\chi_1(\omega), ...,\chi_n(\omega))$ of through flows fulfil the following stochastic balance equations

$$\chi_i = \sum_{j=1}^{n} a_{ij}(\omega)\chi_j(\omega) + F_{io}(\omega)$$

Perturbations in the system structure (in order to improve possible impacts of flows) can be described by some parameters or decision variables $u=(u_1,...,u_l)$ like in section 5.

We can assume that the matrix A as well as the outflows and inflows in or from a process are affected by decisions u (A_{ij} and F_{ij} are functions of u): $A(u,\omega)$, $A_0(u,\omega)$, $F_{0i}(u,\omega)$, $F_{i0}(u,\omega)$, $i=1,...,n$.

Effects of perturbations are described by a number of performance functions or indicators, which may reflect costs, benefits or risks. Each of such a function can be denoted (see section 5) as $f(\chi, A, A_0, F, \omega)$ where χ implicitly depends on u. Expected performance is a function of u:

$$F(u)=E[f(\chi\ (u,\omega\ ),A(u,\omega\ ),A_o(u,\omega\ ),\ F(u,\omega\ ),\omega\ ].$$

Let us notice that the function F(u) may have a rather general structure. For example it may define the probability to exceed ambient standards at monitoring sites (receptors), which might be a risk indicator of constraint (18). For such indicators the performance function has the following form:

$$f=\begin{cases} 1, \ if \ \ \chi_i(u,\omega)>q_i, \ \ for \ \ some \ \ or \ \ all \ \ i\in J, \\ 0, otherwise \end{cases}$$

Such a case of discontinuous function requires special tools (see[13]). Here we discuss only the case of differentiable functions $f(\chi,A,A_0,F,\omega)$(with respect to χ,A,A_0,F).

If there are finite number of "scenarios" ω=1,2,...,N, then the expected performance can be written as

$$F(u)=\sum_{\omega=1}^{N} f(\chi,A,A_0,F,\omega)\rho(\omega)$$

where $\rho(\omega)$ are corresponding probabilities. For small N this problem can be solved by standard optimization techniques.

Unfortunately the combinatorics of multiple uncertainties runs quickly to an astronomic number N, exhausting the possibilities of the conventional optimization tools. In this case F(u) can be minimized only by using the stochastic optimization numerical methods [7] designed for large scale problems and practically arbitrary distributions of random variables.

One approach is based on the calculations of so called stochastic quasi gradients, which are biased or unbiased estimates of the gradient F_u indicating directions of improvements. Formulas of section 5 provide all necessary details.

First of all, from Eq.(19) follows that (under existence of all required derivatives)

$$\frac{\partial f}{\partial u_k}=\sum_{l=1}^{n}\frac{\partial f}{\partial \chi_l}\frac{\partial \chi_l}{\partial u_k}+\sum_{1,i\neq 0}\frac{\partial f}{\partial a_{li}}\frac{\partial a_{li}}{\partial u_k}+\sum_{l=1}^{n}\frac{\partial f}{\partial a_{0l}}\frac{\partial a_{0l}}{\partial u_k}+\sum_{l=1}^{n}\frac{\partial f}{\partial F_{0l}}\frac{\partial F_{0l}}{\partial u_k}$$

where derivatives $\frac{\partial \chi_i}{\partial u_k}$ are calculated according to Eq.(16)

$$\frac{\partial \chi_i}{\partial u_k}=\sum_{l=1}^{n}\frac{\partial (I-A)_{li}^{-1}}{\partial u_k}F_{0l}+\sum_{l=1}^{n}(I-A)_{li}^{-1}\frac{\partial F_{0l}}{\partial u_k}$$

From Eq.(14)

$$\frac{\partial (I-A)_{li}^{-1}}{\partial u_k}=\sum_{s,t\neq 0}\frac{\partial (I-A)_{li}^{-1}}{\partial a_{st}}\frac{\partial a_{st}}{\partial u_k}=$$

$$=\sum_{s,t\neq 0}(I-A)_{ls}^{-1}(I-A)_{ti}^{-1}\frac{\partial a_{st}}{\partial u_k}$$

This calculations can be used for each possible observation of random parameters ω. The stochastic quasi gradient procedure then is described as the following.

Suppose a current set of decision values u is fixed. Generate a possible "scenario" ω by using Monte Carlo simulation.

(i) calculate the random vector

$$\xi=(\frac{\partial f}{\partial u_1},\ldots,\frac{\partial f}{\partial u_n})$$

according to the above outlined formulas for a given u and observed ω. This is an estimate of the gradient $F_u(u)$:

$$F_u(u) = E(\xi|u)$$

where $E(\xi|u)$ is the conditional expectation (conditional for a given u).

(ii) Change the current values of decision variables in the calculated directionξ with a certain step-size and certain devises to maintain the feasibility constraints.

The applicability of such type of procedure follows from general results of stochastic optimization.

Consider now a situation, where the transfer coefficients are random, but the through flows are considered as deterministic. This situation arises in cases when transfer coefficients are calculated with errors. The resulting problems are briefly discussed in [8]. If coefficients of Eq.(6) are random, then a given vector $\chi=(\chi_1,...,\chi_n)$ cannot satisfy this equation for all possible values a_{ij}. The concept of solutions for stochastic a_{ij} may be similar to the concept used in solving overdefined equations.

We can find a solution to the stochastic flow balance equations

$$\chi_i = \sum_{j=1}^{n} a_{ij}(\omega)\chi_j + F_{io}(\omega), \quad i=1,...,n \tag{20}$$

as a vector $\chi=(\chi_1,...,\chi_n)$ minimizing one of the fuctions

$$\begin{aligned} R^1(x) &= E\|\chi - \chi A(\omega) - F(\omega)\|^2 \\ &= E\sum_{i=1}^{n}[(\chi_i - \sum_{j=1}^{n} a_{ji}(\omega)\chi_j - F_{oi}(\omega)]^2 \end{aligned} \tag{21}$$

$$R^2(\chi) = E\sum_{i=1}^{n}\left|(\chi_i - \sum_{j=1}^{n} a_{ji}(\omega)\chi_j - F_{oi}(\omega)\right| \tag{22}$$

$$R^3(\chi) = E\max_i\left|(\chi_i - \sum_{j=1}^{n} a_{ji}(\omega)\chi_j - F_{oi}(\omega)\right| \tag{23}$$

subject to

$$\chi = (\chi_1,\dots,\chi_n) \geq 0 \tag{24}$$

where E is the mathematical expectation symbol.

If a_{ij}, F_{oi} are deterministic then the solution of the flow balance equation (6) or (20) under the assumption of its existence (existence of the structure matrix $(I-A)^{-1}$) is equivalent to the solution of above mentioned minimization problems. Functions R^1, R^2 and R^3 define a fitting measure of a given χ, satisfying (6) against all possible values of a_{ij} and F_{0i}. Properties of solutions defined by functions (20)-(23) are quite different. While the function R^1 defines solutions similar to well known least square estimators , the measure R^2 provides more robustness of the solution to variations of a_{ij}, F_{i0} and R^3 pays attention to extreme values of these parameters.

Here we focus our attention only on solutions defined by $R^1(\chi)$. The important property of a material flow model is the existence of the flow : existence of the nonnegative vector χ (for any nonnegative F) satisfying Eq.(6).

Let us discuss such properties for solutions defined by R^1 without constraints (24). Function $R^1(\chi)$ can be rewritten as

$$E\|\chi-\chi A(\omega)\|^2-2(\chi-\chi\bar{A},\bar{F})+E\|F\|^2=$$
$$=E(\chi(I-A),\chi(I-A))-2(\chi-\chi\bar{A},\bar{F})+E\|F\|^2$$

where $\bar{A}=EA$ and $\bar{F}=EF$.

Each positively defined matrix is represented as the product of CC^T, where C^T is a nondegenerated matrix. Therefore if

$$P_r\{\det(I-A)\neq 0\}=\delta>0,$$

then $R^1(\chi)$ is a strictly concave quadratic function.

Since

$$R^1(\chi)\geq 0$$

then there exists the unique solution χ^* minimizing R^1. It is a nonnegative solution for nonnegative vectors F in the following case.

The solution χ^* satisfies the optimality conditions:

$$R^1_\chi=E[\chi-\chi A(\omega)-F(\omega)](I-A^T(\omega))=0$$

where

$$R^1_\chi=(R^1_{\chi_1},\dots,R^1_{\chi_n})$$

is the gradient of R^1. Let us notice that when ω assumes only a single value (deterministic case) then this equation reduces to the following :

$$[\chi-\chi A-F](I-A^T)=0$$

or the original equation (6) :

$$\chi-\chi A-F=0,$$

when $(I-A)^{-1}$ exists. Suppose

$$v(\omega)=\bar{A}-A,$$

then

$$R^1_\chi(\chi)=E[\chi-\chi A-F](I-\bar{A}^T)+E[\chi-\chi A-F](\bar{A}^T-A^T)=$$
$$(\chi-\chi\bar{A})(I-\bar{A}^T)+\chi Evv^T-\bar{F}(I-\bar{A}^T)=0$$

Assume that $(I-\bar{A})^{-1}$ exists. Then we can conclude that the vector minimizing R^1 satisfies the equation

$$\chi(I-[\bar{A}-Evv^T(I-\bar{A}^T)^{-1}])-\bar{F}=0 \tag{25}$$

This equation is similar to the deterministic Eq.(6) and it is not difficult to derive assumptions insuring the existence of the non negative solution for a non negative F.

For instance, suppose for each i=1,...,n

$$\sum_{j=1}^{n}\bar{a}_{ij}\leq 1,$$

with at least one strong inequality. This is usually assumed for existence of $(1-\bar{A})^{-1}$.

Then the existence of nonnegative solution of Eq. (25) would follow from the assumption

$$\overline{A}^T - E\nu\tilde{\nu}(I-\overline{A})^{-1} \geq 0$$

This assumption is equivalent to the inequality

$$(I-\overline{A})^{-1}_{ij} \sum_l E(\overline{a}_{jl} - a_{jl})^2 \leq \overline{a}_{ji}$$

in the case when vectors $(a_{1i},...,a_{ni})$ are mutually independent. Since usually arcs (j,i) exist only for some j or i, and therefore $\overline{a}_{ji} = 0$ for some i and j, the inequality generally speaking can not be satisfied. This illustrates the essential importance of constraint (24).
The minimization of function (or function R^2, R^3)

$$R^1(x) = E\|\chi - \chi A(\omega) - F(\omega)\|^2 \tag{26}$$

subject to nonnegativity constraints

$$\chi = (\chi_1,\ldots,\chi_n) \geq 0 \tag{27}$$

is a stochastic programming problem. (see [8]) and can be solved by existing methods.

Let us discuss only an approach to minimize R^1, since the discussion of minimization techniques for R^2 and R^3 requires some knowledge of nondifferentiable optimization. One approach is to approximate the expectation $R^1(\chi)$ by sample mean

$$R^1_n(\chi) = \frac{1}{N}\sum_{k=1}^{N}\|\chi - \chi A^k - F^k\|^2$$

and minimize this function subject to nonnegative constraints (27), where A^k, F^k, with k=1,...,N, are independent samples of A and F. Here for the sake of notation simplicity we assume that there is the same number N of observations for each process.
When one of the matrices I-A^k, is a nondegenerate matrix, then R^1_N is a strictly concave function . The solution of this minimization problem provides an estimate to the solution χ^* of the original problem.. It is possible to show that $\chi^N \to \chi^*$ with probability 1 and to derive a rate of convergence. This approach requires the collection of a representative number of observations $A^1,F^1,...;A^N,F^N$ and only then to proceed with the estimation. It may lead to a rather large sample N resulting in a rather complicated problem.
Another solution strategy is to organize an on-line estimation procedure, when a new observation is generated at the current step of the optimization.
Assume that at the initial step k=0, there exists an initial approximate solution $(\chi^0 = (\chi^0_1,\ldots,\chi^0_n) \geq 0$ and an observation A^0, F^0. Suppose that after the k-th step an approximation $\chi^k = (\chi^k_1,\ldots,\chi^k_n)$ is achieved and A^k, F^k are generated. Then the next approximate solution χ^{k+1} is calculated as

$$\chi^{k+1} = \max\{0, \chi^k - \rho_k(\chi^k - \chi^k A^k - F^k)(I-(A^k)^T)\}$$

where ρ_k is a step-size multiplier, for example ρ_k=const./k.

The convergence of the sequence $\{\chi^k\}$ to a solution minimizing the risk functions (21) follows from general results of the stochastic optimization.
There are also other solutions strategies which can be important in the case of dynamic material flow models. For a discussion of some strategies in the case of input-output models see also [9].

7. Conclusion

Industrial metabolism studies aim to identify and asses all possible sources and various pathways of pollution to an "environment". What are the most critical parts of the pollution generating system? What are first priority actions to reduce a possible threat? How do changes of industrial practice, recycling techniques or waste treatment facilities affect storage capacities and outflows to the environment? What is preferable, increase of production costs or clean up? What are the efficiencies of regulatory strategies compared to emission permits, taxes on inputs, taxes on pollution and pollution trade permits? Can we trace effects of such measures through the pollution generating network?

Searching for answers to such policy oriented questions is hopelessly inefficient without the use of an appropriate model as a simulator, since otherwise it requires expensive and dangerous "trial and error" experiments. The model introduced in this paper is very efficient for the comparison of one policy with another. Simply by varying the parameters defining a policy (e.g. the technology of recycling) the simulation shows if policy leads to improvements.

In this paper we have discussed techniques for material flow analysis based on transfer coefficients and steady state performance. These assumptions are essentially used in the Rhine study and the RAINS model (see [3] [5]),where dynamic aspects are in fact analyzed through "slices " of steady state intervals. Irregular dynamically loads may be critically important for modelling of accumulation or storage possibly involving "safety" thresholds or chemical time bomb phenomena (see[10]), where cause and effects are related with some time delay process. It requires appropriate techniques which are not the scope of this paper.

The steady state assumptions are important for analyzing interactions between various parts of the system, its bottlenecks and the sensitivity to changes in processes or connections.

The assumption of fixed transfer cofficients seems to be a rather reasonable approximation for systems where mainly industrial processes are considered, because only technical changes influence these parameters.

The discussed approach requires no more initial data then is usually used in material flows studies: the identification of processes (compartments), calculation of inflows and transfer coefficients between (only) neighbouring processes. The technique then allows the derivation of various consequences of this initial information: the propagation of inflows through all possible paths, the contribution of processes to various throughflows and their effects in order to find the most critical parts of the system for necessary corrections or monitoring.

The described techniques allow also the formulation of various policy oriented optimization and identification and, in particular inverse problems: to identify causes by sampling some consequences.

In section 6 uncertainties and risks involved in material flow analysis are discussed only with respect to the flow estimation and some flow optimization problems.A more general framework is needed for policy oriented comparative studies involving risks and uncertainties of transfer coefficients as well as possible failures and accidential pollution. A dynamic approach in this case enables analysis of stocks and storage processes, limits of "carrying"capacities and investment strategies to anticipate future problems..

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