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On the necessary conditions of optimality of water utilization systems in process plants with multiple contaminants

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Abstract

This paper presents necessary conditions of optimality for multicomponent water allocation systems in refineries and process plants. We extend the necessary conditions of optimality proved for single component by Savelski and Bagajewicz (Chem. Eng. Sci. 55(21) (2000) 5035). In particular, it is shown that at least one component reaches the maximum concentration at the outlet of a freshwater user process. A necessary condition of monotonicity is also proven. In this particular case, monotonicity only holds for certain components called "key" components.

Keywords: Wastewater minimization; Water minimization; Water networks design

1. Introduction

The chemical and petrochemical industry uses substantial amount of water. Wastewater streams containing several contaminants (phenols, sulfides, ammonia, benzene, oil, etc.) create an environmental pollution problem. The background of this problem was discussed and described in detail by several researchers (Takama et al., 1980; Wang and Smith, 1994). A recent review presents a roadmap for efficient installations as well as a discussion of the relevance of the problem (Bagajewicz, 2000). The problem is a particular application of Mass Exchanger Network (MEN) technology and not a separate area of research. The targeting part of the procedure presented by Wang and Smith (1994) is a direct application of mass exchange technology (El-Halwagi and Manousiouthakis, 1989, 1990). Nevertheless, one cannot minimize the visionary work of Prof. Umeda (Takama et al., 1980) for posing the problem and the contributions of Prof. Smith (Wang and Smith, 1994 and following papers).

In a preceding paper, Savelski and Bagajewicz (2000) presented necessary conditions of optimality of this problem. In a follow-up paper, Savelski and Bagajewicz (2001a) presented an algorithmic method to design these systems. The method presented can be implemented by hand and provides one globally optimal solution. The necessary conditions of optimality for single components were also used to obtain a MILP formulation of the problem (Savelski and Bagajewicz, 2001a,b) and to show that several alternative solutions exist. These conditions have been also used to solve the problem of simultaneous allocation of water and heat integration between fresh and wastewater (Bagajewicz et al., 2002).

Superstructure models have been developed to solve this problem. Doyle and Smith (1997) proposed an iterative procedure to solve this bilinearly constrained problem. Alva-Argáez et al. (1998) continued this line of work and proposed solving a two-phase procedure for the solution of a non-convex MINLP. Even after the problem has been successfully solved there is no guarantee about the optimality of the optimum. Finally, Huang et al. (1999) also present a mathematical programming solution of the combined problem of water allocation and treatment. Despite these efforts, there are indications that the multicomponent problem has several suboptimal solutions that are close to the global optimum (Savelski and Bagajewicz, 2000). For this reason, it is important to investigate the properties of this problem, to be able to move away from the straight use of NLP/MINLP solution procedures that can only provide one solution which is not guaranteed optimal,

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into algorithmic procedures that are capable of solving the problem in a robust manner guaranteeing global optimality. *This paper provides the necessary tools to achieve such procedure*.

The paper is organized as follows. Firstly the problem statement is given. Then a few definitions are revisited as well as new ones are provided. This is followed by the necessary conditions. Finally, the conditions are illustrated. We do not present a method to design a water allocation system in this paper.

2. Problem statement

Given a set of water-using/water-disposing processes, it is desired to determine a network of interconnections of water streams among the processes so that the overall fresh water consumption is minimized while the processes receive water of adequate quality. This is what is referred to as the Water/Wastewater Allocation Planning (WAP) problem.

Limits on inlet and an outlet concentration of pollutant are imposed a-priori on each process and a fixed load of contaminants is used. These inlet and outlet concentrations limits account for corrosion, fouling, maximum solubility, etc. Before we discuss our necessary conditions of optimality, some definitions that will be useful later are presented.

Definition: Different types of water-using sets and processes were defined in previous work (Savelski and Bagajewicz, 2000). Fig. 1 illustrates schematically the way these processes are aligned.

- Fresh water user processes (FWU).
- Wastewater user processes (WWU).
- Head processes (H).
- Intermediate wastewater user processes (I).
- Terminal wastewater user processes (T).
- Set of precursors of a process j (P_j).
- Set of receivers of process j (R_j).
- Partial wastewater providers (PWP).
- Total wastewater providers (TWP).

We now introduce a few new definitions:

Component base fresh water: This is the fresh water consumption assuming the maximum outlet concentration is reached.

$$G^w_{j,s} = \frac{L_{j,s}}{C^{\max}_{j,s,\mathrm{out}}}. \quad (1)$$

Key component: Component with the largest $G^w_{j,s}$.

3. Necessary conditions of optimality

The necessary conditions of optimality are presented in a sequence of theorems.

Theorem 1. (Necessary Condition of key component Concentration Decreasing Monotonicity). *If a solution to the WAP is optimal, then at every Partial Wastewater Provider (PWP), the outlet concentrations* of a key component *are not lower than the concentration of the same key component in the combined wastewater stream coming from all the precursors*. Fig. 2 *illustrates the connections of interest*.

In other words, given a process j that satisfies the definition of PWP, that is $F_{j,\mathrm{out}} > 0$, *then* $C_{j,\mathrm{out},k_j} \geqslant C_{P_j,j,k_j}$, *where* C_{P_j,j,k_j} *is the concentration* of the key component of process j *in the combined wastewater of all the precursors*.

Proof. The proof is by contradiction: Assume that $C_{P_j,j,k} > C_{j,k,\mathrm{out}}$. A component mass balance over process j for component s is

$$F_{P_j,j}C_{P_j,j,s} + L_{j,s} = (F_{P_j,j} + F^w_j)C_{j,s,\mathrm{out}} \quad \forall s \in \boldsymbol{C}, \quad (2)$$

where $L_{j,s}$ is the load of component s in process j. Rewriting (2),

$$F^w_j = \frac{L_{j,s}}{C_{j,s,\mathrm{out}}} + \left(\frac{C_{P_j,j,s}}{C_{j,s,\mathrm{out}}} - 1\right) F_{P_j,j}, \quad (3)$$

which is valid for all components.

But, by assumption

$$\left(\frac{C_{P_j,j,k}}{C_{j,k,\mathrm{out}}} - 1\right) > 0. \quad (4)$$

Thus, if $F_{P_j,j}$ (which is positive) is reduced to zero a new fresh water flowrate, $\bar{F}^w_j = L_{j,k}/C_{j,k,\mathrm{out}} < F^w_j$ is obtained, contradicting the hypothesis that the original structure is optimal. To complete the proof one only needs to show that such reduction can be performed without altering any conditions downstream.

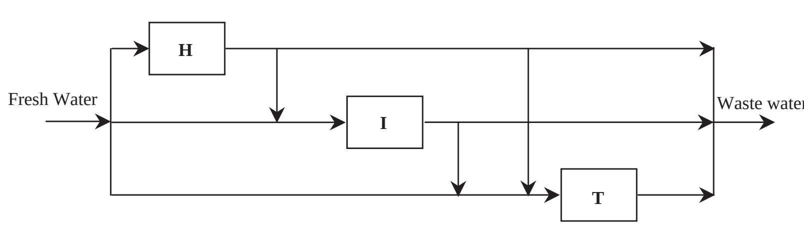

Fig. 1. Schematic representation of a water network.

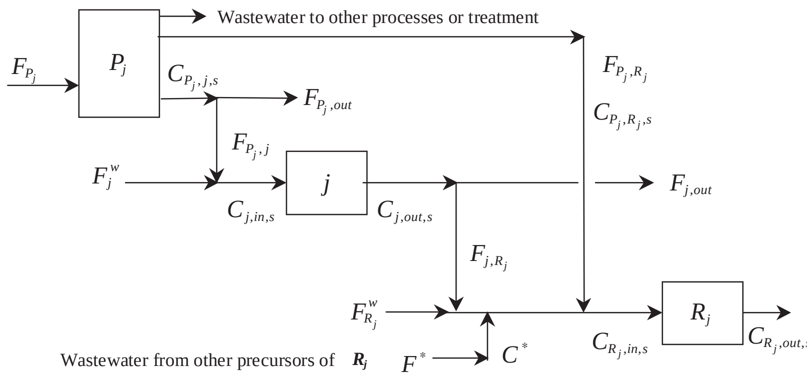

Fig. 2. Precursors and receivers of process j.

We now calculate what is the effect of this change on the rest of the components. The outlet concentrations of component s before and after are obtained from the following manipulations:

$$\begin{aligned} C_{j,s,\mathrm{out}} &= \frac{L_{j,s}}{(F_{P_j,j}+F_j^w)} + \frac{F_{P_j,j}C_{P_j,j,s}}{(F_{P_j,j}+F_j^w)} \\ &\leqslant \frac{L_{j,s}}{F_j^w} + \frac{F_{P_j,j}C_{P_j,j,s}}{(F_{P_j,j}+F_j^w)} \\ &\leqslant \frac{L_{j,s}}{\bar{F}_j^w} + \frac{F_{P_j,j}C_{P_j,j,s}}{(F_{P_j,j}+F_j^w)} \\ &= \bar{C}_{j,s,\mathrm{out}} + \frac{F_{P_j,j}C_{P_j,j,s}}{(F_{P_j,j}+F_j^w)}. \end{aligned} \tag{5}$$

In addition, one can also write

$$\begin{aligned} C_{j,s,\mathrm{out}} &= \frac{\bar{F}_j^w \bar{C}_{j,s,\mathrm{out}}}{(F_{P_j,j}+F_j^w)} + \frac{F_{P_j,j}C_{P_j,j,s}}{(F_{P_j,j}+F_j^w)} \\ &\geqslant \frac{\bar{F}_j^w \bar{C}_{j,s,\mathrm{out}}}{(F_{P_j,j}+F_j^w)}. \end{aligned} \tag{6}$$

Therefore, using (5) and (6):

$$C_{j,s,\mathrm{out}} - \frac{F_{P_j,j}C_{P_j,j,s}}{(F_{P_j,j}+F_j^w)} \leqslant \bar{C}_{j,s,\mathrm{out}} \leqslant \frac{(F_{P_j,j}+F_j^w)}{\bar{F}_j^w} C_{j,s,\mathrm{out}}. \tag{7}$$

In other words, the new concentration can be either higher or lower than the original. Indeed, if $C_{P_j,j,s}$ is zero, then the new outlet concentration will be higher. However, in the case that $C_{P_j,j,s}$ is very high, then it could be lower. We will now prove that it will not be higher than the maximum value $C_{j,s,\mathrm{out}}^{\max}$.

By definition of key component

$$\frac{L_{j,k}}{C_{j,k,\mathrm{out}}^{\max}} \geqslant \frac{L_{j,s}}{C_{j,s,\mathrm{out}}^{\max}}. \tag{8}$$

Therefore,

$$\frac{L_{j,k}}{C_{j,k,\mathrm{out}}} \geqslant \frac{L_{j,k}}{C_{j,k,\mathrm{out}}^{\max}} \geqslant \frac{L_{j,s}}{C_{j,s,\mathrm{out}}^{\max}}. \tag{9}$$

Then, the new concentration of component s is

$$\bar{C}_{j,s,\mathrm{out}} = \frac{L_{j,s}}{\bar{F}_j^w} = \frac{L_{j,s}}{(L_{j,k}/C_{j,k,\mathrm{out}})} \leqslant C_{j,s,\mathrm{out}}^{\max}, \tag{10}$$

which makes the new outlet feasible. Now feasibility downstream needs to be restored.

In the case of one component, two cases were possible:

(a) Process j could still supply all the necessary wastewater to the set $\boldsymbol{R}_j$, that is, $\bar{F}_j^w \geqslant F_{j,R_j}$. In the case of one component the conditions downstream were not affected and no further analysis was needed.
(b) Process j cannot deliver the same amount of wastewater to the set $\boldsymbol{R}_j$, that is, $\bar{F}_j^w < F_{j,R_j}$. Thus, feasibility conditions downstream of process j need to be restored as well.

However, for multiple components, there is an increase in the concentration of non-key components and therefore feasibility conditions downstream of process j need to be restored regardless of the case. Since it has been proven that the fresh water consumption of process j can be reduced to its minimum by eliminating $F_{P_j,j}$, downstream feasibility may be restored by reusing part or all this available wastewater. Fig. 3 shows the new situation.

In the case of one component, we only needed to analyze case (b) and then, we considered the following cases:

(b.1) Feasibility can be restored by reusing a flowrate $\bar{Q}_{P_j,R_j}$, which has the same concentration $C_{P_j,j}$.

(b.2) The new flowrate $\bar{Q}_{P_j,R_j}$ does not exceed the previous value used $F_{P_j,j}$. That is $\bar{Q}_{P_j,R_j} \ni (0, F_{P_j,j}]$.

These statements were proven true in Theorem 1 for a single component case. These conditions guaranteed fresh water reduction while maintaining downstream feasibility at the inlet of $\boldsymbol{R}_j$.

We now explore how new conditions to maintain downstream feasibility are needed for a multicomponent case.

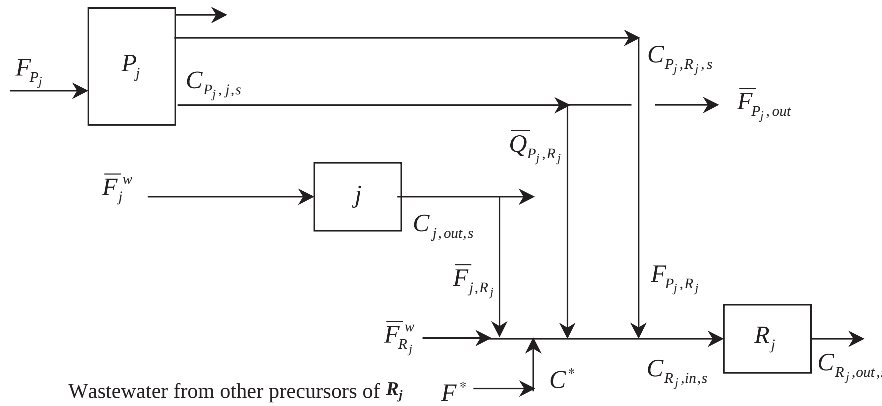

Fig. 3. Monotonicity restoration.

(b.1) *Feasibility can be restored using* $\bar{Q}_{P_j,R_j}$: Assume the following new set of downstream feasibility conditions at the inlet of $\boldsymbol{R}_j$:

$$F_{R_j} = \bar{F}_{R_j} \tag{11}$$

and

$$\bar{f}_{j,R_j,s} = f_{j,R_j,s}, \quad s = k_j, \quad \text{auxiliary component.} \tag{12}$$

Rewriting (11) we obtain:

$$F_{R_j} = F_{j,R_j} + F_{P_j,R_j} + F_{R_j}^w + F^*$$
$$= \bar{F}_{j,R_j} + \bar{Q}_{P_j,R_j} + F_{P_j,R_j} + \bar{F}_{R_j}^w + F^* = \bar{F}_{R_j} \tag{13}$$

after simplifying common terms and rearranging, we get

$$\Delta F_{R_j}^w = F_{j,R_j} - \bar{F}_{j,R_j} - \bar{Q}_{P_j,R_j}. \tag{14}$$

Moreover, using (2) written in terms of the key-component and using (3) we can write

$$\Delta F_j^w = \bar{F}_j^w - F_j^w = (1 - \alpha_{k_j}) F_{P_j,j}, \tag{15}$$

where $\alpha_{k_j} = C_{P_j,j,k}/C_{j,k,\text{out}} > 1$.

Now, we can write

$$\Delta W = \Delta F_j^w + \Delta F_{R_j}^w. \tag{16}$$

Substituting Eqs. (14) and (15) into Eq. (16) we obtain

$$\Delta W = (1 - \alpha_{k_j}) F_{P_j,j} + F_{j,R_j} - \bar{F}_{j,R_j} - \bar{Q}_{P_j,R_j}. \tag{17}$$

In the one component problem, $\bar{F}_{j,R_j} = \bar{F}_j^w$ and $\bar{Q}_{P_j,R_j}$ was easily replaced. In the multiple component case, all it is known is that $\bar{F}_{j,R_j} \leqslant \bar{F}_j^w$ and that $\bar{Q}_{P_j,R_j} \leqslant F_{P_j}$.

Writing (12) for the key and the auxiliary component and then rearranging, we get

$$\bar{F}_{j,R_j} = (F_{j,R_j} C_{j,\text{out},k_j} - \bar{Q}_{P_j,R_j} C_{P_j,j,k_j}) \frac{1}{\bar{C}_{j,\text{out},k_j}} \tag{18}$$

and

$$\bar{F}_{j,R_j} = (F_{j,R_j} C_{j,\text{out,aux}_j} - \bar{Q}_{P_j,R_j} C_{P_j,j,\text{aux}_j}) \frac{1}{\bar{C}_{j,\text{out,aux}_j}}. \tag{19}$$

A mass balance performed on any component i gives

$$\bar{C}_{j,\text{out},i} = \frac{L_{j,i}}{\bar{F}_j^w}. \tag{20}$$

Equating (18) and (19), and replacing $\bar{C}_{j,\text{out},i}$ by Eq. (20), we obtain

$$(F_{j,R_j} C_{j,\text{out},k_j} - \bar{Q}_{P_j,R_j} C_{P_j,j,k_j})$$
$$= \frac{L_{j,k_j}}{L_{j,\text{aux}_j}} (F_{j,R_j} C_{j,\text{out,aux}_j} - \bar{Q}_{P_j,R_j} C_{P_j,j,\text{aux}_j}). \tag{21}$$

Rearranging,

$$\bar{Q}_{P_j,R_j} = F_{j,R_j} \delta, \tag{22}$$

where

$$\delta = \frac{\left(C_{j,\text{out,aux}_j} (L_{j,k_j}/L_{j,\text{aux}_j}) - C_{j,\text{out},k_j}\right)}{\left(C_{P_j,j,\text{aux}_j} (L_{j,k_j}/L_{j,\text{aux}_j}) - C_{P_j,j,k_j}\right)}. \tag{23}$$

Using (18), (20), (22) and (23) we can obtain an expression for $\bar{F}_{j,R_j}$:

$$\bar{F}_{j,R_j} = \frac{F_{j,R_j} \bar{F}_j^w C_{j,\text{out},k_j}}{L_{j,k_j}} [1 - \alpha_{k_j} \delta]. \tag{24}$$

Substituting Eqs. (22) and (24) into Eq. (17) and using (15) to replace $\bar{F}_j^w$ in (24), we get

$$\Delta W = (1 - \alpha_{k_j}) F_{P_j,j} + F_{j,R_j}(1 - \delta)$$
$$- \frac{F_{j,R_j} C_{j,\text{out},k_j}}{L_{j,k_j}} [1 - \alpha_{k_j} \delta][F_j^w + (1 - \alpha_{k_j}) F_{P_j,j}]. \tag{25}$$

A key-component mass balance on j, $(F_{P_j,j} + F_j^w) C_{j,\text{out},k_j} = F_{P_j,j} C_{P_j,j,k_j} + L_{j,k_j}$, can now be used to remove F_j^w from (25)

$$\Delta W = (1 - \alpha_{k_j}) F_{P_j,j} + F_{j,R_j}(1 - \delta)$$
$$- \frac{F_{j,R_j} C_{j,\text{out},k_j}}{L_{j,k_j}} [1 - \alpha_{k_j} \delta]$$
$$\times \left[F_{P_j,j} \alpha_{k_j} + \frac{L_{j,k_j}}{C_{j,\text{out},k_j}} - F_{P_j,j} + (1 - \alpha_{k_j}) F_{P_j,j} \right]. \tag{26}$$

Simplifying (26), we obtain

$$\Delta W = (1-\alpha_{k_j})(F_{P_j,j} - \delta F_{j,R_j}). \tag{27}$$

We now need to obtain an expression for δ as a function of $F_{P_j,j}$ and F_{j,R_j}.

Rewriting (23),

$$\delta = \frac{C_{j,\text{out},k_j}}{C_{P_j,j,k_j}} \frac{\left((C_{j,\text{out,aux}_j}/C_{j,\text{out},k_j})\varepsilon - 1\right)}{\left((C_{P_j,j,\text{aux}_j}/C_{P_j,j,k_j})\varepsilon - 1\right)}, \tag{28}$$

where $\varepsilon = L_{j,k_j}/L_{j,\text{aux}_j}$.

We write component mass balances for k_j and aux_j, those are

$$F_j C_{j,\text{out},k_j} = F_{P_j,j} C_{P_j,j,k_j} + L_{j,k_j} \tag{29}$$

and

$$F_j C_{j,\text{out,aux}_j} = F_{P_j,j} C_{P_j,j,\text{aux}_j} + L_{j,\text{aux}_j}. \tag{30}$$

Rearranging (29) and (30), then dividing them through, we obtain

$$\frac{C_{P_j,j,\text{aux}_j}}{C_{P_j,j,k_j}} = \frac{F_j C_{j,\text{out,aux}_j} - L_{j,\text{aux}_j}}{F_j C_{j,\text{out},k_j} - L_{j,k_j}}. \tag{31}$$

Multiplying first both sides of (31) by ε then subtracting 1 from each side and finally rearranging the r.h.s., we get

$$\frac{C_{P_j,j,\text{aux}_j}}{C_{P_j,j,k_j}}\varepsilon - 1 = \frac{\left((F_j C_{j,\text{out,aux}_j}/L_{j,\text{aux}_j}) - 1\right)}{\left((F_j C_{j,\text{out},k_j}/L_{j,k_j}) - 1\right)} - 1 \tag{32}$$

or

$$\frac{C_{P_j,j,\text{aux}_j}}{C_{P_j,j,k_j}}\varepsilon - 1 = \frac{\left((F_j C_{j,\text{out,aux}_j}/L_{j,\text{aux}_j}) - (F_j C_{j,\text{out},k_j}/L_{j,k_j})\right)}{\left((F_j C_{j,\text{out},k_j}/L_{j,k_j}) - 1\right)}. \tag{33}$$

Rewriting (29),

$$\frac{F_j C_{j,\text{out},k_j}}{L_{j,k_j}} - 1 = \frac{F_j C_{P_j,j,k_j}}{L_{j,k_j}}. \tag{34}$$

Substituting Eq. (34) into Eq. (33) and rearranging,

$$\frac{C_{P_j,j,\text{aux}_j}}{C_{P_j,j,k_j}}\varepsilon - 1 = \frac{F_j C_{j,\text{out},k_j}\left((C_{j,\text{out,aux}_j}/C_{j,\text{out},k_j})\varepsilon - 1\right)}{F_{P_j,j} C_{P_j,j,k_j}}. \tag{35}$$

Substituting Eq. (35) into Eq. (28) and rearranging, we obtain

$$\delta = \frac{F_{P_j,j}}{F_j}. \tag{36}$$

Using (36) into (27), we obtain the final expression for ΔW,

$$\Delta W = (1-\alpha_{k_j}) F_{P_j,j} \left(1 - \frac{F_{j,R_j}}{F_j}\right) < 0. \tag{37}$$

Remark. Eq. (37) depends only on the original flowrates and α_{k_j}, that is, the auxiliary component does not appear. Therefore, any component can be used as auxiliary, which means that all contaminants satisfy (11). From this and in virtue of (12), it can be concluded that $\bar{C}_{R_n,\text{in},s} = C_{R_n,\text{in},s}\ \forall s \in \boldsymbol{C}$.

(b.2) *As it was done for the single-contaminant case, we need to show that* $\bar{Q}_{P_j,R_j}$ *is feasible*: Combining (22) and (36), we obtain

$$\bar{Q}_{P_j,R_j} = F_{j,R_j} \frac{F_{P_j,j}}{F_j} = \frac{1}{1 + (F_{j,\text{out}}/F_{j,R_j})} F_{P_j,j}. \tag{38}$$

Therefore, $\bar{Q}_{P_j,R_j} \leqslant F_{P_j,j}$. □

Corollary 1. *If for a given process j a solution is optimal and* $C_{P_j,j,k_j} = C_{j,\text{out},k_j}$, *then the solution is degenerated in the sense that any wastewater send to process j from its precursors does not alter the total water intake.*

Proof. When $C_{P_j,j,k_j} = C_{j,\text{out},k_j}$, (2) states that $L_{j,k_j} = F_j^w C_{j,\text{out},k_j}$. That is the interconnection between the set $\boldsymbol{P}_j$ and process j is of no practical use when seeking a decrease in F_j^w. □

Remark. If $F_{j,\text{out}} = 0$ then from (37) $\Delta W = 0$. However, this does not mean that the proposed solution before and after are equivalent. In fact, the following example shows that neither is optimal.

Consider the three-process flowsheet shown in Fig. 4. Process 2 reuses water from process 1 violating the monotonicity of the key-component (b). Process 3 reuses all the water of process 2, making $F_{2,\text{out}} = 0$. Fig. 5 shows the alternative solution where monotonicity has been restored and the fresh water consumption remains unchanged. Finally, Fig. 6 shows the network that realizes the minimum freshwater usage. This network allows for an increase in the outlet concentrations of the contaminants. Therefore, if process 3 were not a terminal process then the lower-consumption network (Fig. 6) would be infeasible.

Theorem 2. (Necessary Condition of Maximum Concentration for Head Processes). *If a solution of the WAP problem is optimal, then the outlet concentration of the key-component of a Partial Provider Head Process is equal to its maximum.*

Proof. The theorem is proved by contradiction. Assume

$$C_{h,\text{out},k_h} < C_{h,\text{out},k_h}^{\max}. \tag{39}$$

Writing a mass balance for the key-component, we obtain:

$$L_{h,k_h} = F_h^w C_{h,\text{out},k_h} = \bar{F}_h^w C_{h,\text{out},h_k}^{\max}. \tag{40}$$

Then, in virtue of (39)

$$\bar{F}_h^w = \frac{C_{h,\text{out},k_h}}{C_{h,\text{out},h_k}^{\max}} F_h^w < F_h^w. \tag{41}$$

Therefore, the fresh water consumption is reduced by exiting at the maximum outlet concentration of the key-component.

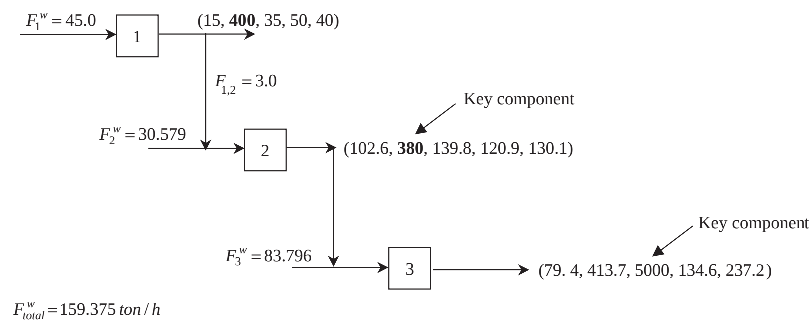

Fig. 4. Monotonicity violation in process 2.

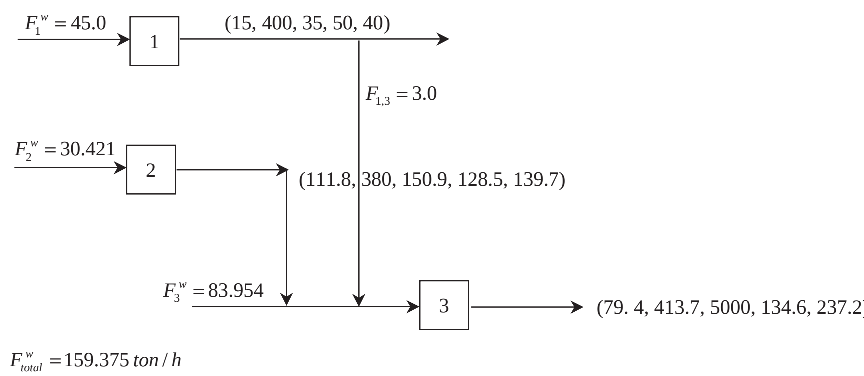

Fig. 5. Monotonicity restoration with $\Delta W = 0$.

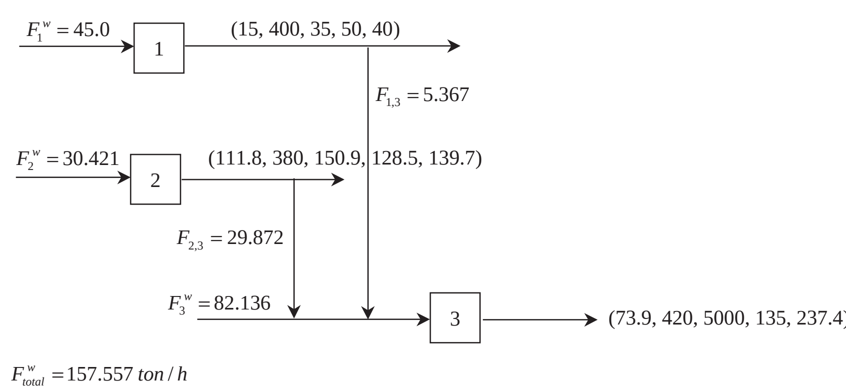

Fig. 6. Optimal water network.

Actually, the theorem is self-proved by the key-component definition. In addition, because of this definition, the outlet concentrations of the non-key components remain feasible as previously shown by Eq. (10).

In the case where the water is reused downstream, (41) still constitutes a proof if one is able to show that after the reduction, the conditions downstream remain feasible. Fig. 7 shows downstream reuse of a head process wastewater outlet. For this purpose, consider now the following downstream feasibility conditions:

$$\text{(a)} \quad \bar{F}_{R_{h_i}} = F_{R_{h_i}} \quad \forall R_{h_i} \in \boldsymbol{R}_h, \tag{42}$$

$$\text{(b)} \quad \bar{f}_{h,R_{h_i},b_{R_{h_i}}} = f_{h,R_{h_i},b_{R_{h_i}}} \quad \forall R_{h_i} \in \boldsymbol{R}_h \text{ and for some } b_{R_{h_i}}. \tag{43}$$

Now we need to show that:

$$\text{(A)} \quad \sum_{R_{h_i}} \bar{F}_{h,R_{h_i}} \leqslant \sum_{R_{h_i}} F_{h,R_{h_i}},$$

$$\text{(B)} \quad \Delta W < 0,$$

$$\text{(C)} \quad \bar{C}_{R_{h_i},s} \leqslant C_{R_{h_i},s}.$$

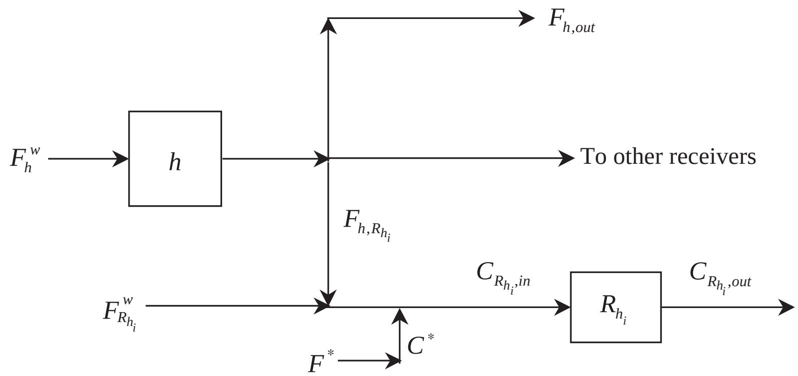

Fig. 7. A head process and its receivers.

Without loss of generality, we take any process R_{h_i} of the set of receivers $\boldsymbol{R}_h$.

Part (A): From (42) we have:

$$\bar{F}_{h,R_{h_i}} + \bar{F}^w_{R_{h_i}} = F_{h,R_{h_i}} + F^w_{R_{h_i}}. \tag{44}$$

Using (43),

$$\bar{F}_{h,R_{h_i}} \bar{C}_{h,\text{out},b_{R_{h_i}}} = F_{h,R_{h_i}} C_{h,\text{out},b_{R_{h_i}}}, \tag{45}$$

$$\bar{F}_{h,R_{h_i}} = \beta_{b_{R_{h_i}}} F_{h,R_{h_i}}, \tag{46}$$

where $\beta_{b_{R_{h_i}}} = C_{h,\text{out},b_{R_{h_i}}}/\bar{C}_{h,\text{out},b_{R_{h_i}}} \leqslant 1$, therefore

$$\bar{F}_{h,R_{h_i}} \leqslant F_{h,R_{h_i}}. \tag{47}$$

Since flowrates cannot be take negative values and in virtue of (47), we obtain

$$\sum_{R_{h_i}} \bar{F}_{h,R_{h_i}} \leqslant \sum_{R_{h_i}} F_{h,R_{h_i}}. \tag{48}$$

Part (B):

$$\Delta W = \Delta F^w_h + \sum_{R_{h_i}} \Delta F^w_{R_{h_i}}. \tag{49}$$

From (41)

$$\Delta F^w_h = \bar{F}^w_h - F^w_h = -(1-\beta_{k_h})F^w_h. \tag{50}$$

From (44)

$$\Delta F^w_{R_{h_i}} = \bar{F}^w_{R_{h_i}} - F^w_{R_{h_i}} = F_{h,R_{h_i}} - \bar{F}_{h,R_{h_i}} \quad \forall R_{h_i} \in \boldsymbol{R}_h. \tag{51}$$

Substituting Eq. (46) into Eq. (51), we obtain

$$\Delta F^w_{R_{h_i}} = (1-\beta_{b_{R_{h_i}}})F_{h,R_{h_i}} \quad \forall R_{h_i} \in \boldsymbol{R}_h. \tag{52}$$

Substituting Eqs. (50) and (52) into Eq. (49), we get

$$\Delta W = -(1-\beta_{k_h})F^w_h + \sum_{R_{h_i}} (1-\beta_{b_{R_{h_i}}})F_{h,R_{h_i}}. \tag{53}$$

We now substitute (41) and (46) in the definition of $\bar{F}_{h,\text{out}}$, as follows:

$$\bar{F}_{h,\text{out}} = \bar{F}^w_h - \sum_{R_{h_i}} \bar{F}_{h,R_{h_i}} = \beta_{k_h} F^w_h - \sum_{R_{h_i}} \beta_{b_{R_{h_i}}} F_{h,R_{h_i}}. \tag{54}$$

Now, the values of $\beta_{b_{R_{h_i}}}$ and β_{k_h} are most probable all different but we can still analyze a limiting case by taking the larger possible value of β and use it as upper limit (β^{UL}).

Replacing all β values by β^{UL} in (54), we can write

$$\bar{F}_{h,\text{out}} \leqslant \beta^{UL}\left(F^w_h - \sum_{R_{h_i}} F_{h,R_{h_i}}\right) = \beta^{UL} F_{h,\text{out}}. \tag{55}$$

Therefore,

$$\bar{F}_{h,\text{out}} \leqslant F_{h,\text{out}}. \tag{56}$$

Rewriting (53), we obtain

$$\Delta W = \left(-F^w_h + \sum_{R_{h_i}} F_{h,R_{h_i}}\right) + \left(\beta_{k_h} F^w_h - \sum_{R_{h_i}} \beta_{b_{R_{h_i}}} F_{h,R_{h_i}}\right)$$
$$= -F_{h,\text{out}} + \bar{F}_{h,\text{out}} \leqslant 0. \tag{57}$$

Part C: A generic component mass balance performed in the inlet of R_{h_i} reads:

$$\bar{C}_{R_{h_i},\text{in},s}(\bar{F}^w_{R_{h_i}} + \bar{F}_{h,R_{h_i}}) = \bar{F}_{h,R_{h_i}} \bar{C}_{h,\text{out},s}, \tag{58}$$

where s can be any component.

Using (44), we can write

$$\bar{C}_{R_{h_i},\text{in},s} = \frac{\bar{F}_{h,R_{h_i}} \bar{C}_{h,\text{out},s}}{(F^w_{R_{h_i}} + F_{h,R_{h_i}})}. \tag{59}$$

Using (46) to replace $\bar{F}_{h,R_{h_i}}$, we get

$$\bar{C}_{R_{h_i},\text{in},s} = \frac{\beta_{b_{R_{h_i}}} F_{h,R_{h_i}}}{(F^w_{R_{h_i}} + F_{h,R_{h_i}})} \bar{C}_{h,\text{out},s}. \tag{60}$$

Using first a mass balance for contaminant s in the head process and then a mass balance for the key-component, we obtain

$$\bar{C}_{R_{h_i},\text{in},s} = \frac{\beta_{b_{R_{h_i}}} F_{h,R_{h_i}}}{(F^w_{R_{h_i}} + F_{h,R_{h_i}})} C_{h,\text{out},s} \frac{\bar{F}^w_h}{F^w_h}$$
$$= \frac{\beta_{b_{R_{h_i}}} F_{h,R_{h_i}}}{(F^w_{R_{h_i}} + F_{h,R_{h_i}})} C_{h,\text{out},s} \frac{C_{h,\text{out},k_h}}{C^{\max}_{h,\text{out},k_h}} \tag{61}$$

or

$$\bar{C}_{R_{h_i},\text{in},s} = \beta_{b_{R_{h_i}}} \frac{C_{h,\text{out},k_h}}{C^{\max}_{h,\text{out},k_h}} C_{R_{h_i},\text{in},s}. \tag{62}$$

Now, $\beta_{b_{R_{h_i}}} \leqslant 1$ and $C_{h,\text{out},k_h}/C^{\max}_{h,\text{out},k_h} \leqslant 1$, therefore, their product is lower or equal to one as well. Consequently, $\bar{C}_{R_{h_i},\text{in},s} \leqslant C_{R_{h_i},\text{in},s}$, which is what it needed to be proved. □

Theorem 3. (Necessary Condition of Maximum Concentration for Intermediate Processes). *If the solution of the WAP problem is optimal then the outlet concentration of at least one component of an Intermediate Process reaches its maximum.*

Proof. Assume that neither $C_{p,j,\text{in}}$ nor $C_{p,j,\text{out}}$ are at their maximum possible values for all components.

In the proof of this theorem for the single component case, we proved that an increase in the flowrate from the precursors ($\boldsymbol{P}_j$) of process j reduces the total water intake. This increase results first in a reduction in fresh water intake of process j. As a result of this increase, either the single component would reach its maximum inlet concentration (CASE I), or the all the water from the precursors is used up (CASE II). A condition is imposed in this reduction so that the outlet concentration of process j remains constant. This reduction, does not alter conditions downstream at the inlet of the receivers of process j ($\boldsymbol{R}_j$).

In case I, the maximum outlet concentration is achieved by now reducing the flowrate from the precursors ($\boldsymbol{P}_j$) of process j simultaneously with the fresh water usage to process j. The bulk of the proof relies then in proving that the feasibility of the network of receivers can be maintained by increasing the fresh water sent to the receivers in such a way that the flowrate and concentration of the inlet stream to these receivers are the same. The proof also shows that this increase in fresh water sent to the receivers is smaller that the savings obtained by reducing the intake of process j.

In Case II, the fresh water intake of process j is reduced until, either the maximum inlet concentration is reached first, or the maximum outlet concentration is reached first. In the latter case, the proof is complete and the proof of feasibility downstream is provided, whereas in the former case the rest of the proof is similar to Case I.

We will now provide a proof for the multicomponent case based on the same strategy.

Let $\hat{F}_{P_j} = F_{P_j,\text{out}} + F_{P_j,j}$. Assume now that all this flow is sent to process j, accompanied by a new flow of freshwater $\hat{F}^w_j$. Then:

$$\hat{C}_{p,j,\text{in}} = \frac{\hat{F}_{P_j} C_{p,P_j,j}}{\hat{F}_{P_j} + \hat{F}^w_j}, \tag{63}$$

$$L_{p,j} = (\hat{F}_{P_j} + \hat{F}^w_j)(\hat{C}_{p,j,\text{out}} - \hat{C}_{p,j,\text{in}}). \tag{64}$$

We choose $\hat{F}^w_j$ such that $\hat{C}_{p,j,\text{out}} \leqslant C_{p,j,\text{out}} \quad \forall p$ and $\hat{C}_{t,j,\text{out}} = C_{t,j,\text{out}}$, for some component t called here binding component. We will prove now that this component t satisfies the following inequality:

$$\frac{L_{t,j}}{C_{t,P_j,j}} \leqslant \frac{L_{p,j}}{C_{p,P_j,j}} \quad \forall p. \tag{65}$$

Indeed,

$$\hat{C}_{p,j,\text{out}} = \frac{\hat{F}_{P_j,j} C_{p,P_j} + L_{p,j}}{\hat{F}_{P_j,j} + \hat{F}^w_j}. \tag{66}$$

Then,

$$\frac{\hat{C}_{p,j,\text{out}}}{\hat{C}_{t,j,\text{out}}} = \frac{\hat{C}_{p,j,\text{out}}}{C_{t,j,\text{out}}} = \frac{\hat{F}_{P_j,j} C_{p,P_j} + L_{p,j}}{\hat{F}_{P_j,j} C_{t,P_j} + L_{t,j}}. \tag{67}$$

To prove the assertion, all one needs to prove is that the derivative of the above quotient is negative, that is

$$\frac{\partial}{\partial \hat{F}_{P_j,j}} \left[\frac{\hat{C}_{p,j,\text{out}}}{\hat{C}_{t,j,\text{out}}} \right] = \frac{\partial}{\partial \hat{F}_{P_j,j}} \left[\frac{\hat{F}_{P_j,j} C_{p,P_j} + L_{p,j}}{\hat{F}_{P_j,j} C_{t,P_j} + L_{t,j}} \right]$$
$$= C_{p,P_j} C_{t,P_j} \left[\frac{L_{t,j}}{C_{t,P_j}} - \frac{L_{p,j}}{C_{p,P_j}} \right] \leqslant 0. \tag{68}$$

In other words, as $\hat{F}_{P_j,j}$ increases and $\hat{F}^w_j$ is picked to maintain $C_{t,j,\text{out}}$ constant, then the concentration of the other components is smaller, i.e. $\hat{C}_{p,j,\text{out}} \leqslant C_{p,j,\text{out}}$. We recognize that this is true for all the range of $\hat{F}_{P_j,j}$.

Alternative proof. Consider first

$$\frac{L_{p,j}}{C_{p,P_j,j}} = \frac{(F_{P_j,j} + F^w_j) C_{p,j,\text{out}} - F_{P_j,j} C_{p,P_j,j}}{C_{p,P_j,j}}$$
$$= \frac{(F_{P_j,j} + F^w_j) C_{p,j,\text{out}}}{C_{p,P_j,j}} - F_{P_j,j} \tag{69}$$

therefore substituting Eq. (69) into Eq. (65)

$$\frac{C_{t,j,\text{out}}}{C_{t,P_j,j}} \leqslant \frac{C_{p,j,\text{out}}}{C_{p,P_j,j}} \quad \forall p. \tag{70}$$

Now, since

$$\hat{F}^w_j = \frac{\hat{F}_{P_j,j} C_{t,P_j} + L_{t,j}}{C_{t,j,\text{out}}} - \hat{F}_{P_j,j}. \tag{71}$$

We substitute it in Eq. (66) to get:

$$\hat{C}_{p,j,\text{out}} = \frac{\hat{F}_{P_j,j} C_{p,P_j} + L_{p,j}}{(\hat{F}_{P_j,j} C_{t,P_j} + L_{t,j}/C_{t,j,\text{out}})}$$
$$= C_{t,j,\text{out}} \frac{\hat{F}_{P_j,j} C_{p,P_j} + L_{p,j}}{\hat{F}_{P_j,j} C_{t,P_j} + L_{t,j}}$$
$$= C_{t,j,\text{out}} \frac{F_{P_j,j} C_{p,P_j} + \Delta F_{P_j,j} C_{p,P_j} + L_{p,j}}{F_{P_j,j} C_{t,P_j} + \Delta F_{P_j,j} C_{t,P_j} + L_{t,j}}$$

$$= C_{t,j,\text{out}} \frac{(F_{P_j,j} + F_j^w)C_{p,j,\text{out}} + \Delta F_{P_j,j} C_{p,P_j}}{(F_{P_j,j} + F_j^w)C_{t,j,\text{out}} + \Delta F_{P_j,j} C_{t,P_j}}$$

$$= C_{p,j,\text{out}} \frac{(F_{P_j,j} + F_j^w) + \Delta F_{P_j,j} \dfrac{C_{p,P_j}}{C_{p,j,\text{out}}}}{(F_{P_j,j} + F_j^w) + \Delta F_{P_j,j} \dfrac{C_{t,P_j}}{C_{t,j,\text{out}}}}$$

$$\leqslant C_{p,j,\text{out}} \tag{72}$$

the last step being true because $C_{p,P_j}/C_{p,j,\text{out}} \leqslant C_{t,P_j}/C_{t,j,\text{out}}$ as given in Eq. (70). □

We recognize two conditions:

Case I: $\hat{C}_{k,j,\text{in}} \geqslant C^{\max}_{k,j,\text{in}}$ for at least one component k. In this case, we will prove the theorem by first proving that the inlet concentration of at least one component of process j can be made equal to its maximum, with a reduction of the water intake of process j. Finally, we will show that the total fresh water intake of the system can be subsequently lowered by maximizing the outlet concentration of process j.

Case II: $\hat{C}_{p,j,\text{in}} < C^{\max}_{p,j,\text{in}}\ \forall p$. In this case, we will prove that the outlet concentration of process j can be made equal to its maximum, with a reduction of the total water intake.

Case I: Let k be a component for which $\hat{C}_{k,j,\text{in}} \geqslant C^{\max}_{k,j,\text{in}}$. All the other components have smaller concentration, i.e. $\hat{C}_{p,j,\text{in}} \leqslant \hat{C}_{k,j,\text{in}}\ \forall p$. Then, starting from (64)

$$\begin{aligned} L_{k,j} &= (\hat{F}_{P_j} + \hat{F}_j^w)(\hat{C}_{k,j,\text{out}} - \hat{C}_{j,\text{in}}) \\ &\leqslant (\hat{F}_{P_j,j} + \hat{F}_j^w)(\hat{C}_{k,j,\text{out}} - C^{\max}_{k,j,\text{in}}) \\ &= \frac{\hat{F}_{P_j,j} C_{k,P_j,j}}{\hat{C}_{k,j,\text{in}}}(\hat{C}_{k,j,\text{out}} - C^{\max}_{k,j,\text{in}}) \\ &\leqslant \frac{\hat{F}_{P_j,j} C_{k,P_j,j}}{C^{\max}_{k,j,\text{in}}}(\hat{C}_{k,j,\text{out}} - C^{\max}_{k,j,\text{in}}). \end{aligned} \tag{73}$$

Therefore,

$$\left(\frac{\hat{C}_{k,j,\text{out}}}{C^{\max}_{k,j,\text{in}}} - 1\right) \geqslant \frac{L_{k,j}}{\hat{F}_{P_j} C_{k,P_j,j}}, \tag{74}$$

which is an inequality that will be useful later. Eq. (74) does not hold for the components that do not satisfy the inequality $\hat{C}_{p,j,\text{in}} \geqslant C^{\max}_{k,j,\text{in}}$.

We will prove that the water consumption can be reduced by increasing $F_{P_j,j}$ until the maximum inlet concentration is reached for at least one component r. The fresh water consumption will be adjusted to maintain the binding component t at the outlet at its current values, that is, $\bar{C}_{t,j,\text{out}} = C_{t,j,\text{out}}$ where $\bar{C}_{t,j,\text{out}}$ indicate the outlet concentration at the new condition and $\bar{F}_{P_j,j}$ and $\bar{F}_j^w$ are the new flowrates. As proved above all the rest of the components will have a lower concentration. From a balance in the inlet node, we obtain:

$$C^{\max}_{k,j,\text{in}} = \frac{\bar{F}_{P_j,j} C_{k,P_j,j}}{\bar{F}_{P_j,j} + \bar{F}_j^w}, \tag{75a}$$

$$C^{\max}_{p,j,\text{in}} \geqslant \frac{\bar{F}_{P_j,j} C_{p,P_j,j}}{\bar{F}_{P_j,j} + \bar{F}_j^w}. \tag{75b}$$

In addition a component balance on process j gives:

$$C_{p,j,\text{out}} = \frac{\bar{F}_{P_j,j} C_{p,P_j,j} + L_{p,j}}{\bar{F}_{P_j,j} + \bar{F}_j^w}. \tag{76}$$

Divide Eq. (76) by Eq. (75b) for the key component s

$$\frac{C_{s,j,\text{out}}}{C^{\max}_{s,j,\text{in}}} \leqslant \frac{\bar{F}_{P_j,j} C_{s,P_j,j} + L_{s,j}}{\bar{F}_{P_j,j} C_{s,P_j,j}} = \left(1 + \frac{L_{s,j}}{\bar{F}_{P_j,j} C_{s,P_j,j}}\right). \tag{77}$$

Rearranging

$$\bar{F}_{P_j,j} \leqslant \frac{L_{s,j}}{C_{s,P_j,j}} \frac{1}{(C_{s,j,\text{out}}/C^{\max}_{s,j,\text{in}} - 1)}, \tag{78}$$

where $\bar{C}_{s,j,\text{in}} \leqslant C^{\max}_{s,j,\text{in}}$. Then

$$\bar{F}_{P_j,j} = \frac{L_{s,j}}{C_{s,P_j,j}} \frac{1}{(C_{s,j,\text{out}}/\bar{C}_{s,j,\text{in}} - 1)} \tag{79}$$

for some $\bar{C}_{s,j,\text{in}} \leqslant C^{\max}_{s,j,\text{in}}$. Repeating the same procedure for the original conditions one obtains:

$$F_{P_j,j} = \frac{L_{s,j}}{C_{s,P_j,j}} \frac{1}{(C_{s,j,\text{out}}/C_{s,j,\text{in}} - 1)} \tag{80}$$

and since $C_{s,j,\text{in}} < \bar{C}_{s,j,\text{in}}$, we obtain

$$F_{P_j,j} < \bar{F}_{P_j,j}. \tag{81}$$

Also, rearranging (75b) for the key component

$$\bar{F}_j^w \leqslant \bar{F}_{P_j,j}\left(\frac{C_{s,P_j,j}}{C^{\max}_{s,j,\text{in}}} - 1\right), \tag{82}$$

which can be written as follows:

$$\bar{F}_j^w = \bar{F}_{P_j,j}\left(\frac{C_{s,P_j,j}}{\bar{C}_{s,j,\text{in}}} - 1\right). \tag{83}$$

Similarly

$$F_j^w = F_{P_j,j}\left(\frac{C_{s,P_j,j}}{C_{s,j,\text{in}}} - 1\right). \tag{84}$$

Finally, substituting Eq. (79) into Eq. (82) we obtain

$$\bar{F}_j^w = \frac{L_{s,j}}{C_{s,P_j,j}} \frac{(C_{s,P_j,j}/\bar{C}_{s,j,\text{in}} - 1)}{(C_{s,j,\text{out}}/\bar{C}_{s,j,\text{in}} - 1)}. \tag{85}$$

Similarly, using a set of balances for the assumed optimal condition the following is obtained:

$$F_j^w = \frac{L_{s,j}}{C_{s,P_j,j}} \frac{(C_{r,P_j,j}/C_{r,j,\text{in}} - 1)}{(C_{s,j,\text{out}}/C_{s,j,\text{in}} - 1)}. \tag{86}$$

Starting from $C_{s,j,\text{in}} < \bar{C}_{s,j,\text{in}}$ and multiplying by $(C_{s,P_j,j} - C_{s,j,\text{out}})$, which is negative (key component theorem), one can go through the same steps as in the case of the single component case to conclude that

$$\frac{(C_{s,P_j,j}/\bar{C}_{s,j,\text{in}} - 1)}{(C_{s,j,\text{out}}/\bar{C}_{s,j,\text{in}} - 1)} < \frac{(C_{s,P_j,j}/C_{s,j,\text{in}} - 1)}{(C_{s,j,\text{out}}/C_{s,j,\text{in}} - 1)}, \tag{87}$$

which leads to $\bar{F}_j^w < F_j^w$.

To complete the proof it is necessary to prove that:

(a) $\bar{F}_{P_j,\text{out}} \geqslant 0$, which is part of the assumption made at the beginning of the proof.
(b) $\bar{F}_{j,R_j} = F_{j,R_j}$ is feasible, that is, the conditions downstream do not need to change. In other words, a reduction in fresh water to process j, does not reduce the outlet of this process below what it was sent to its receivers.

Part a: $\bar{F}_{P_j,\text{out}} \geqslant 0$

$$\bar{F}_{P_j,j} = \frac{L_{k,j}}{C_{k,P_j,j}} \frac{1}{(C_{k,j,\text{out}}/\bar{C}_{k,j,\text{in}} - 1)}. \tag{88}$$

From (79)

$$\frac{L_{k,j}}{C_{k,P_j,j}} = \bar{F}_{P_j,j}\left(\frac{C_{k,j,\text{out}}}{\bar{C}_{k,j,\text{in}}} - 1\right). \tag{89}$$

But k is such that $\hat{C}_{k,j,\text{in}} \geqslant C_{k,j,\text{in}}^{\max}$, and substitution in Eq. (74) gives.

$$\frac{\bar{F}_{P_j,j}}{\hat{F}_{P_j}} \leqslant 1, \tag{90}$$

which completes the proof.

Part b: $\bar{F}_{j,R_j} = F_{j,R_j}$ is feasible.

A component mass balance over process j reads:

$$F_j C_{s,j,\text{out}} = L_{s,j} + F_{P_j,j} C_{s,P_j,j}, \tag{91}$$

$$\bar{F}_j C_{s,j,\text{out}} = L_{s,j} + \bar{F}_{P_j,j} C_{s,P_j,j}. \tag{92}$$

Subtracting Eq. (91) from Eq. (92) and dividing by $C_{j,\text{out}}$

$$(\bar{F}_j - F_j) = (\bar{F}_{P_j,j} - F_{P_j,j}) \frac{C_{s,P_j,j}}{C_{s,j,\text{out}}}. \tag{93}$$

Since $(\bar{F}_{P_j,j} - F_{P_j,j}) > 0$, then $(\bar{F}_j - F_j) > 0$. Therefore, F_{j,R_j} can be always kept constant by increasing $F_{j,\text{out}}$. To complete the proof we need to show that the maximum outlet concentration of process j can be reached and that this will produce a fresh water intake reduction. The increase in outlet concentration need to be accompanied by new conditions to maintain feasibility downstream at the inlet of the receivers from process j. This can be obtained by keeping F_{R_j} constant and $\bar{\bar{C}}_{p,R_j,\text{in}} \leqslant C_{p,R_j,\text{in}}$ and proving that there will be sufficient wastewater for reuse, that is $\bar{\bar{F}}_j^w + \bar{\bar{F}}_{P_j,j} \geqslant \bar{\bar{F}}_{j,R_j}$. The fresh water decrease can be achieved by reducing $\bar{F}_{P_j,j}$ and $\bar{F}_j^w$ simultaneously. To guarantee that the overall fresh water consumption will be reduced the excess availability at process j, defined as $(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j})$, will be bypassed to the set $\boldsymbol{R}_j$. The new situation is shown in Fig. 8.

Now, from (79) we can write,

$$\bar{\bar{F}}_{P_j,j} = \frac{L_{s,j}}{C_{s,P_j,j}} \frac{1}{(C_{s,j,\text{out}}^{\max}/\bar{C}_{s,j,\text{in}} - 1)}. \tag{94}$$

Comparing (79) and (94) it clearly turns out that $\bar{\bar{F}}_{P_j,j} < \bar{F}_{P_j,j}$.

The new fresh water supply to process j, $\bar{\bar{F}}_j^w$, can be calculated using Eq. (82), that is:

$$\bar{\bar{F}}_j^w = \bar{\bar{F}}_{P_j,j}\left(\frac{C_{s,P_j j}}{\bar{C}_{s,j,\text{in}}} - 1\right) < \bar{F}_j^w. \tag{95}$$

All we need to show now is that these fresh water savings are not overcome by any necessary increased in $F_{R_j}^w$. Consider a component mass balance of process j at outlet conditions before and after the fresh water reduction.

$$C_{s,j,\text{out}}(\bar{F}_{P_j,j} + \bar{F}_j^w) = \bar{F}_{P_j,j} C_{s,P_j,j} + L_{s,j}, \tag{96}$$

$$C_{s,j,\text{out}}^{\max}(\bar{\bar{F}}_{P_j,j} + \bar{\bar{F}}_j^w) = \bar{\bar{F}}_{P_j,j} C_{s,P_j,j} + L_{s,j}. \tag{97}$$

Equating (96) and (97) by $L_{s,j}$ and rearranging, we obtain:

$$\bar{\bar{F}}_j^w = \alpha_s \bar{F}_{P_j,j} + \alpha_s \bar{F}_j^w - \bar{\bar{F}}_{P_j,j} - \beta_s(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}), \tag{98}$$

where $\alpha_s = \dfrac{C_{s,j,\text{out}}}{C_{s,j,\text{out}}^{\max}}$ and $\beta_s = \dfrac{C_{s,P_j,j}}{C_{s,j,\text{out}}^{\max}}$.

Then,

$$\Delta F_j^w = \bar{\bar{F}}_j^w - \bar{F}_j^w = \alpha_s \bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j} - \beta_s(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) - (1 - \alpha_s)\bar{F}_j^w. \tag{99}$$

Downstream feasibility is maintained by imposing:

$$C_{p,R_j,\text{in}} = \frac{\bar{F}_{j,R_j} C_{p,j,\text{out}} + F_{P_j,R_j} C_{p,P_j,R_j} + F^* C_p^*}{\bar{F}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{F}_{R_j}^w}$$
$$\geqslant \frac{\bar{\bar{F}}_{j,R_j} \bar{\bar{C}}_{p,j,\text{out}} + F_{P_j,R_j} C_{P_j,R_j} + F^* C_p^* + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) C_{p,P_j,j}}{\bar{\bar{F}}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{\bar{F}}_{R_j}^w + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j})} \tag{100}$$

and

$$\bar{F}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{F}_{R_j}^w = \bar{\bar{F}}_{j,R_j} + F_{P_j,R_j} + F^* + \bar{\bar{F}}_{R_j}^w + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \tag{101}$$

There will be one component m that satifies the equality in Eq. (100). Simplifying common terms on both sides of (101), we get

$$\bar{F}_{j,R_j} + \bar{F}_{R_j}^w = \bar{\bar{F}}_{j,R_j} + \bar{\bar{F}}_{R_j}^w + (\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \tag{102}$$

Using (101) into (100) written for the component m that satisfies the equality and simplifying, we obtain

$$\bar{\bar{F}}_{j,R_j} = \alpha_m \bar{F}_{j,R_j} - \beta_m(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}), \tag{103}$$

where $\alpha_m = C_{m,j,\text{out}}/\bar{\bar{C}}_{m,j,\text{out}} < 1$ (trivial) and $\beta_m = C_{m,P_j,j}/\bar{\bar{C}}_{m,j,\text{out}}$.

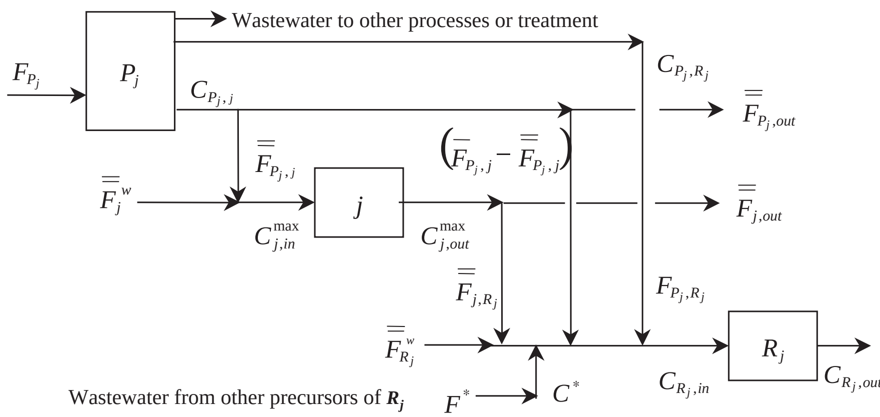

Fig. 8. Maximum inlet and outlet concentrations are reached.

Using (102) and (103) we can write:

$$\Delta F_{R_j}^w = \bar{\bar{F}}_{R_j}^w - \bar{F}_{R_j}^w = (1-\alpha_m)\bar{F}_{j,R_j} -(1-\beta_m)(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}). \quad (104)$$

Finally, combining (99) and (100), we obtain

$$\Delta W = \Delta F_j^w + \Delta F_{R_j}^w = (1-\alpha_m)(\bar{F}_{j,R_j} - \bar{F}_j^w - \bar{F}_{P_j,j}) \leqslant 0. \quad (105)$$

To finish the proof we need to show that under the new conditions there is enough wastewater to send from process j to the set of processes $\boldsymbol{R}_j$. That is, $\bar{\bar{F}}_j^w + \bar{\bar{F}}_{P_j,j} \geqslant \bar{\bar{F}}_{j,R_j}$.

A total mass balance on process j reads:

$$\bar{F}_j^w + \bar{F}_{P_j,j} = \bar{F}_{j,R_j} + \bar{F}_{j,\text{out}}. \quad (106)$$

Then, we can write that

$$\bar{F}_j^w + \bar{F}_{P_j,j} \geqslant \bar{F}_{j,R_j}. \quad (107)$$

Adding $\bar{\bar{F}}_{P_j,j}$ to both sides of (98) and rearranging, we obtain

$$\bar{\bar{F}}_j^w + \bar{\bar{F}}_{P_j,j} + \beta_s(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) = \alpha_s(\bar{F}_{P_j,j} + \bar{F}_j^w). \quad (108)$$

Multiplying both sides of Eq. (107) by α and comparing with (108), we can write

$$\bar{\bar{F}}_j^w + \bar{\bar{F}}_{P_j,j} + \beta_s(\bar{F}_{P_j,j} - \bar{\bar{F}}_{P_j,j}) \geqslant \alpha_s \bar{F}_{j,R_j}. \quad (109)$$

Finally, by Eq. (103) we obtain

$$\bar{\bar{F}}_j^w + \bar{\bar{F}}_{P_j,j} \geqslant \bar{\bar{F}}_{j,R_j}. \quad \square \quad (110)$$

Corollary 1. *If an Intermediate Process j is a Total Wastewater Provider, then any solution having $C_{s,j,\text{out}} \in [C_{s,R_j,\text{in}}, C_{s,j,\text{out}}^{\max}]$ is also optimal with the same consumption.*

Proof. When process j is a TWP then $\bar{F}_{j,\text{out}} = 0$, by Eq. (105) we have $\Delta W = 0$. This means that a degenerated solution has been found. □

Corollary 2. *In CASE I, it is also a necessary condition of optimality that the Intermediate Process j reaches its inlet maximum concentration.*

Proof. Assume the starting solution is such that the outlet concentration of process j is already at its maximum. Then, following exactly the same proof as depicted by Eqs. (75)–(87) but replacing $C_{s,j,\text{out}}^{\max}$ by $C_{s,j,\text{out}}$, $C_{r,j,\text{in}}^{\max}$ can be reached without altering $C_{s,j,\text{out}}^{\max}$. The latter added to the fact that F_{j,R_j} can be kept constant (as shown in part b) guarantees downstream feasibility. □

Case II: Outlet concentration binding condition

$$\left(\frac{C_{p,j,\text{out}}}{C_{p,j,\text{in}}^{\max}} - 1\right) < \frac{L_{p,j}}{\hat{F}_{P_j} C_{p,P_j,j}} \quad \text{for all } p. \quad (111)$$

In this case, an increase in $F_{P_j,j}$ to increase $C_{p,j,\text{in}}$ to its maximum is not possible without violating feasibility.

Assume that $F_{P_j,j}$ is increased to its possible maximum value of $F_{P_j,j}^{\oplus}$ corresponding to $F_{P_j,\text{out}} = 0$. The new situation is shown in Fig. 9. The new inlet concentration in process j is $C_{p,j,\text{in}}^{\oplus} > C_{p,j,\text{in}}$.

We will now prove that it is possible to further reduce water consumption by reducing $F_j^{\oplus_w}$. As a result either maximum inlet or outlet concentration will be reached first and no further water reduction will be possible. This increase needs to be accompanied by conditions to maintain feasibility downstream at the inlet of the receivers from process j. As it was done in CASE I, feasibility can be obtained by keeping F_{R_j} constant and $\bar{C}_{p,R_j,\text{in}} \leqslant C_{R_j,\text{in}}$ while proving that there will be sufficient wastewater for reuse, that is $\bar{F}_j^{\oplus_w} + \hat{F}_{P_j} \geqslant \bar{F}_{j,R_j}$.

We will have then two different possibilities:

(a) A reduction of the fresh water flowrate, $F_j^{\oplus_w}$ will make the outlet concentration reach its maximum before the inlet does. $\bar{C}_{s,j,\text{out}} = C_{s,j,\text{out}}^{\max}$ and $\bar{C}_{s,j,\text{in}} < C_{s,j,\text{in}}^{\max}$.
(b) The inlet maximum is reached first.

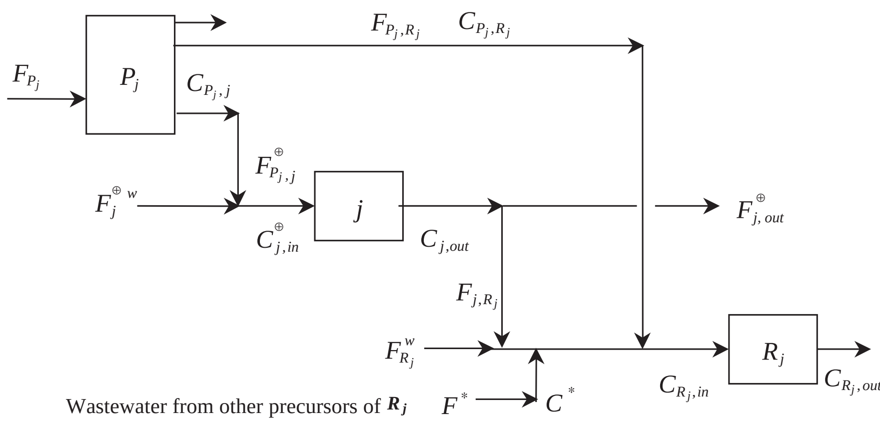

Fig. 9. Reuse of wastewater from the precursors of process j is maximized.

The change in total water intake for both cases is

$$\Delta W = (\bar F^w_{R_j} - F^w_{R_j}) + (\bar F_j^{\oplus w} - F_j^{\oplus w}). \tag{112}$$

(a) $\bar C_{s,j,\mathrm{out}} = C^{\max}_{s,j,\mathrm{out}}$ and $\bar C_{s,j,\mathrm{in}} < C^{\max}_{s,j,\mathrm{in}}$.

Performing mass balances on the component before and after the fresh water flow reduction, we obtain:

$$F^{\oplus}_{P_j,j} C_{s,P_j,j} + L_{s,j} = (F^{\oplus}_{P_j,j} + F_j^{\oplus w}) C_{s,j,\mathrm{out}}, \tag{113}$$

$$F^{\oplus}_{P_j,j} C_{s,P_j,j} + L_{s,j} = (F^{\oplus}_{P_j,j} + \bar F_j^{\oplus w}) C^{\max}_{s,j,\mathrm{out}}. \tag{114}$$

Equating the r.h.s. of these balances and using the fact that $F_{P_j,\mathrm{out}} = 0$, i.e., $F^{\oplus}_{P_j,j} = \hat F_{P_j}$

$$\bar F_j^{\oplus w} = \left(\frac{C_{s,j,\mathrm{out}}}{C^{\max}_{s,j,\mathrm{out}}}\right) F_j^{\oplus w} - \left(1 - \frac{C_{s,j,\mathrm{out}}}{C^{\max}_{s,j,\mathrm{out}}}\right) \hat F_{P_j}$$
$$= \alpha_s F_j^{\oplus w} - (1-\alpha_s)\hat F_{P_j}, \quad 0 < \alpha < 1, \tag{115}$$

where $\alpha_s = C_{s,j,\mathrm{out}}/C^{\max}_{s,j,\mathrm{out}}$.

From (115) we write

$$\bar F_j^{\oplus w} - F_j^{\oplus w} = -(1-\alpha_s)(F_j^{\oplus w} + \hat F_{P_j}). \tag{116}$$

We now calculate $(\bar F^w_{R_j} - F^w_{R_j})$.

Recalling that $C_{R_j,\mathrm{in}}$ and F_{R_j} remain constant, we can write:

$$F^w_{R_j} + F_{j,R_j} + F_{P_j,R_j} + F^*$$
$$= \bar F^w_{R_j} + \bar F_{j,R_j} + F_{P_j,R_j} + F^*, \tag{117}$$

$$C_{m,R_j,\mathrm{in}} = \frac{F_{j,R_j} C_{m,j,\mathrm{out}} + F_{P_j,R_j} C_{m,P_j,R_j} + F^* C^*_m}{F^w_{R_j} + F_{j,R_j} + F_{P_j,R_j} + F^*}$$
$$= \frac{\bar F_{j,R_j} \bar C_{m,j,\mathrm{out}} + F_{P_j,R_j} C_{m,P_j,R_j} + F^* C^*_m}{\bar F^w_{R_j} + \bar F_{j,R_j} + F_{P_j,R_j} + F^*}. \tag{118}$$

Rearranging (118) and using (117) we obtain:

$$\bar F_{j,R_j} = \frac{C_{m,j,\mathrm{out}}}{\bar C_{m,j,\mathrm{out}}} F_{j,R_j} = \alpha_m F_{j,R_j}. \tag{119}$$

Substituting in (117) and rearranging we get:

$$\bar F^w_{R_j} - F^w_{R_j} = F_{j,R_j}(1-\alpha_m) \tag{120}$$

and therefore:

$$\Delta W = (\bar F^w_{R_j} - F^w_{R_j}) + (\bar F_j^{\oplus w} - F_j^{\oplus w})$$
$$= (1-\alpha_m)(F_{j,R_j} - F_j^{\oplus w} - F^{\oplus}_{P_j,j}) \leqslant 0. \tag{121}$$

To finish the proof we need to show that under the new conditions there is enough wastewater to send from process j to the set of processes $\boldsymbol{R}_j$. That is: $\bar F_j^{\oplus w} + \hat F_{P_j} \geqslant \bar F_{j,R_j}$.

Add $\hat F_{P_j}$ to both sides of (115) to obtain:

$$\bar F_j^{\oplus w} + \hat F_{P_j} = \alpha_m (F_j^{\oplus w} + \hat F_{P_j}). \tag{122}$$

But

$$F_j^{\oplus w} + \hat F_{P_j} = F_{j,R_j} + F^{\oplus}_{j,\mathrm{out}}. \tag{123}$$

Thus, since

$$F^{\oplus}_{j,\mathrm{out}} \geqslant 0. \tag{124}$$

We have

$$F_j^{\oplus w} + \hat F_{P_j} \geqslant F_{j,R_j}. \tag{125}$$

And therefore

$$\bar F_j^{\oplus w} + \hat F_{P_j} = \alpha_m (F_j^{\oplus w} + \hat F_{P_j}) \geqslant \alpha F_{j,R_j}. \tag{126}$$

From Eq. (119) we obtain

$$\bar F_j^{\oplus w} + \hat F_{P_j} \geqslant \bar F_{j,R_j}. \quad \square \tag{127}$$

(b) $C_{s,j,\mathrm{out}} < C^{\max}_{s,j,\mathrm{out}}$ and $C_{s,j,\mathrm{in}} = C^{\max}_{s,j,\mathrm{in}}$.

Since reducing only the fresh water intake of process j cannot render the maximum outlet concentration without violating feasibility, we need to proceed exactly the same way we did in CASE I and reduce both, $F_j^{\oplus_w}$ and $F_{P_j,j}^{\oplus}$. The proof is not different from the one in CASE I (for $r=s$), the same group of Eqs. (94)–(105) are used to prove the theorem and then (106)–(110) are used to complete the feasibility proof. Thus $\Delta W \leqslant 0$. □

Corollary 3. *If an Intermediate Process j is a Total Wastewater Provider, then any solution having* $C_{s,j,\text{out}} \in [C_{s,R_j,\text{in}}, C_{s,j,\text{out}}^{\max}]$ *is also optimal with the same consumption.*

Proof. When process j is a TWP then $F_{j,\text{out}}^{\oplus} = 0$, by Eq. (121) we have $\Delta W = 0$. This means that a degenerated solution has been found. □

Example: We resort to a few published solutions to show that these conditions hold. Consider the example presented by Wang and Smith (1994). Table 1shows the limiting data of this problem.

The minimum fresh water consumption reported is 105.6 ton/h. Process 1 is a head process and the mass loads are such that all three component exit at the maximum possible concentration. The key components of processes 2 and 3 are components B and C, respectively. The realizing network is shown in Fig. 10.

Table 1
Example problem from Wang and Smith (1994)

Process	Contaminant	Mass load (kg/h)	$C_{\text{in}}^{\max}$ (ppm)	$C_{\text{out}}^{\max}$ (ppm)
1	A	0.675	0	15
	B	18.0	0	400
	C	1.575	0	35
2	A	3.4	20	120
	B	414.8	300	12,500
	C	4.59	45	180
3	A	5.6	120	220
	B	1.4	20	45
	C	520.8	200	9,500

Note that:

- That the monotonicity of component B in process 2 and the monotonicity of component C in process 3 are satisfied.
- Both processes 2 and 3 have components B and C at their maximum possible outlet concentrations.

4. Conclusions

Necessary conditions of optimality for water utilization systems with multiple pollutants have been derived. Summarizing, these conditions establish that if a system is optimum, freshwater user processes have at least one component reaching its maximum concentration. Monotonicity conditions have also been derived. These correspond to special components called key components. These necessary conditions will be used in future work to develop an algorithmic procedure to design these systems.

Notation

C	concentration of contaminant, ppm
f	component flowrate, g/h
F	water flowrate, ton/h

Subscripts

in	at inlet
out	at outlet
j	process j
P_j	precursors of j
R_j	receivers of j

Superscripts

min	minimum
max	maximum
*	additional sources
w	fresh water

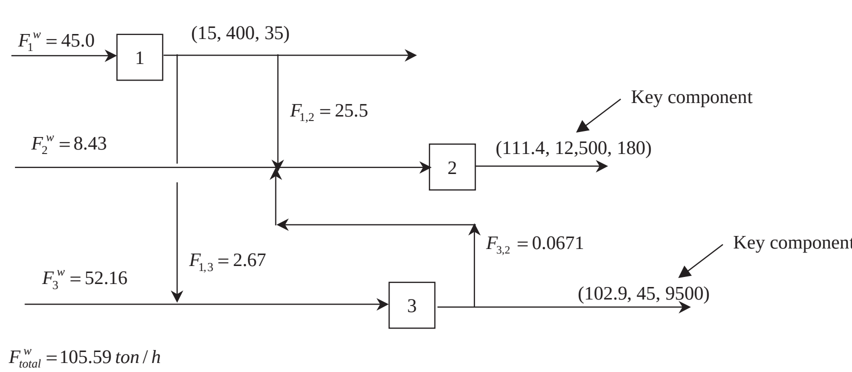

Fig. 10. Water network for minimum intake.

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