



Accumulation of dissolved and colloidal material in papermaking—Application to simulation

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ABSTRACT

Closure of water circuits in papermaking is of vital importance for achieving a more sustainable and economic manufacturing of paper. The most important limiting factor for a further closure is the accumulation of dissolved and colloidal materials (DCM). The extent to which DCM can become enriched in the water depends not only on how many times water is reused but also on the degree to which this matter becomes reattached to the fibers and other solid components of the paper furnish. This study analyzes the accumulation of the most typical contaminants in newsprint (NP) and light weight coated (LWC) paper production. Results show that the release of DCM depends on the present contaminant load in the waters: higher at low contaminant load and lower at high contaminant load. A simulation was carried out to analyze the differences between assuming a constant and a variable release of contaminants to waters. Important differences were observed, especially at low fresh water consumption for those species with a major affinity for the fibers.

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1. Introduction

The reduction of fresh water consumption is very important in the pulp and paper industry for reducing its environmental impact and energy consumption, while at the same time costs are reduced due to savings in freshwater, effluent treatment and disposal costs [1]. In an “open” water system, there is a continuous and substantial purge of contaminants from the system. However, as the mill closes the water systems, there is a considerable accumulation of suspended and dissolved and colloidal material (DCM). While suspended solids are removed in conventional clarification systems, DCM is almost completely recirculated, being necessary the use of internal water treatments and optimized water networks for a further reduction of fresh water consumption [2–5]. The extent to which such materials can become enriched in the white water depends not only on how many times the same process water is reused but also on the degree of adsorption onto the fibers and other solid components of the paper furnish [6,7]. When present at sufficient concentrations, DCM negatively affects the production due to lower retention, increased deposition, foaming, higher biological activity and corrosion [8–11]. Furthermore, DCM also impair

the physical properties of paper and alter the quality of the final product due to the presence of dirt, specks or holes [12–14].

The sources of DCM are the recovered paper, the process and product chemicals and the fresh water, being the recovered paper the main contributor [15]. In fact, the design of new printing and converting products, e.g. environmental benign adhesives, for reducing the contaminant load coming with the recovered paper, is of growing interest [16,17]. The first step in the process, the pulping stage, is critical for the release of contaminants. During pulping, contaminants such as foils, stickies and printing inks are separated from the fibers, and then removed by different stages in the deinking line. To facilitate the separation of the contaminants pulping chemicals such as caustic soda, sodium silicate, hydrogen peroxide and soap are used. Unfortunately, these chemicals will also contribute to a higher release of DCM [18].

Some authors have tried to assess the influence of the reduction of fresh water consumption on the accumulation of contaminants in the water circuits but these studies are limited in terms of the number of the analytical parameters measured [19–22]. This study provides a characterization of the influence of the reduction of fresh water consumption on the main contaminants of interest to papermakers, considering both inorganic and organic contaminants. Furthermore, two types of paper products have been analyzed: newsprint (NP) and light weight coated (LWC).

The second part of this study is the implementation of the results in a simulation of the papermaking process using a commercial software, focusing on the pulping stage. Simulation can be

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used as a very useful and cost-effective tool for prediction of the consequences associated with the process changes necessary for achieving a further closure of the water loops [23]. Although there are references of the simulation of the release of a contaminant during pulping and other process stages, in most of the cases the release of the contaminant or its partitioning between the different output streams in the stage is assumed to be constant [21,24]; this is the type of model used in most available pulp and paper simulation software. However, results indicate that, normally, the release of a contaminant decreases with the degree of contamination of the waters and, consequently, the application of these models cannot be securely extrapolated to operating conditions very different from the current practice such as high closure conditions, and for which there is very little data applicable to commercial production operations [25]. This study will provide the necessary information for obtaining the “release curves” of the most detrimental contaminants in papermaking related to the level of contaminants in the waters, for its application in commercial software and consequently, for obtaining more accurate process simulations.

An accumulation factor (AF) and a release factor (RF) have been introduced in this study with the aim of characterizing the accumulation tendency of the different contaminants. AF analyzes the total increase in the concentration of a specific contaminant through several cycles of accumulation while the RF analyzes the differences between the release of the contaminant in the first cycle of accumulation and the latest cycle of accumulation, where the contaminant load of the waters is maximum. The relation between these two factors for the analyzed contaminants is also shown.

2. Methodology

2.1. Influence of closure on DCM accumulation

Accumulation of DCM in water circuits has been studied by the disintegration of recycled NP and LWC paper, without printing, in consecutive steps reusing the waters from the previous cycle. Disintegration was carried out at 5% consistency (100 g paper in 2 L), at ambient temperature, for 10 min at 3000 rpm. A 692 disintegrator, supplied by ISP S.L (Spain), was used. pH varied between 7.6 and 7.9 in the case of NP paper and between 8.0 and 8.2 for LWC paper. After disintegration, the pulp was filtered in a Büchner funnel with an ALBET 420 paper filter (nominal pore size 60–65 μm), obtaining approximately 1.7 L of filtrate in each case with DCM representing between 86% and 99% of total solids. The effect of the filter pad has been considered equally in all the samples by obtaining always the same filtrate volume. The filtered waters from the different disintegrations in each cycle were mixed and used for the following step. Due to the loss of water in the filter pad and the need of avoiding the use of fresh water for the following disintegrations which could cause shocks in pH, conductivity, cationic demand, etc., the scheme showed in Fig. 1 was followed. As it can be seen in Fig. 1, a total of 36 disintegrations were necessary for the simulation of 8 accumulation cycles at 100% closure degree: eight same disintegrations where carried out in tap water for obtaining after filtration with Büchner funnel enough volume of cycle 1 waters (C1) for the next cycle of accumulation, seven disintegrations where carried out using C1 waters and new paper for obtaining, after Büchner filtration, enough volume of cycle 2 waters (C2) for next cycle of accumulation, etc. Equivalent values of fresh water consumption in these cycles ranged from 20 m^3/t (C1) to 2.5 m^3/t (C8): in each recycling cycle additional 100 g paper is disintegrated in the same waters which were used in the previous cycle. DCM fraction of the filtered waters has been isolated by further filtration of the Büchner filtrate with a 0.45 μm PTFE syringe filter.

Analytical parameters measured to quantify the contamination load in the different recycling cycles are: (a) general: pH, cationic demand, total solids, suspended solids and dissolved solids (measured directly in the Büchner filtrates); (b) organic contaminants: chemical oxygen demand (COD) and total organic carbon (TOC) (measured in the DCM fraction); (c) inorganic contaminants: conductivity, alkalinity, hardness (Ca and Mg), sulphates, nitrates, phosphates, chlorides and metals (Na, K, Fe, Mn, Co, Zn and Cu) (measured in the DCM fraction, except for conductivity and alkalinity, measured in the Büchner filtrates). Term dissolved is used to describe the measurements carried out in the DCM fraction of the waters.

2.2. Process simulation

With the data obtained at lab-scale, a simplified simulation of a paper mill has been carried out using a commercial software available for the simulation of the paper and board industry, called FlowMac[®], based on the Extend[®] platform (www.papermac.se). This software allows including a constant inlet concentration of each tracer, e.g. COD, TOC, sulphates, etc., in the raw materials as the recovered paper or the fresh water, treating them in an independent way in the blocks simulating the different unit operations. This can ease the development of black box environments in which the main objective is the characterization of the behaviour of a specific contaminant. In our work, an improvement has been added to this software, considering a variable inlet concentration of each tracer in the recovered paper depending on the process water contaminant load. This implies that the release of a specific contaminant from the recovered paper is not constant. Therefore, a new code has been added to the existing blocks to continuously calculate the value of each tracer by tailor-made equations depending on the existing concentration of each contaminant in the water circuit.

In the developed simulation, there are two inputs to the process: the fresh water and the stock supply (recovered paper). In this study, the recovered paper is maintained at a constant level: 521 kg/min, equivalent to a consumption of 750 t/d of recovered paper, which would produce around 600 t/d of final product (yield \approx 80%). The fresh water consumption is varied between 521 and 10,417 L/min to consider fresh water consumptions ranging from 1 to 20 m^3/t . The proportion of the specific contaminants that are incorporated into the water circuits has been defined in these two inputs. In the case of fresh water, the concentration of contaminants is constant and it was calculated from the analysis of the tap water used in the disintegrations at lab-scale. In the case of the recovered paper, the release of a specific contaminant is calculated considering the present concentration of this contaminant in the circuits.

Recovered paper and fresh water are mixed in a tank block (continuous-stirred tank reactor), simulating the water circuits of the whole mill. After this tank, the final paper product and the white waters are separated by the definition of a reject ratio for the fibers, fines and fillers. It is also possible to define a reject ratio for the specific contaminants analyzed. In our study, a 99% of the contaminant load is with the process water, and only 1% with the final product (as a basic assumption). After this separation, process waters are further separated with a static separator, in which it has been defined that a 10% of the waters leave the process (to a wastewater treatment plant) and the remaining 90% is recirculated into the process, being added to the mixing tank. New fresh water and recovered paper are mixed together with the process water recirculated in the previous cycle in the mixing tank. After a number of cycles, the values of the specific contaminants in the mixing tank (water circuits), reach the steady state. The concentration of these contaminants for the different fresh water consumptions analyzed is the result of the simulation.

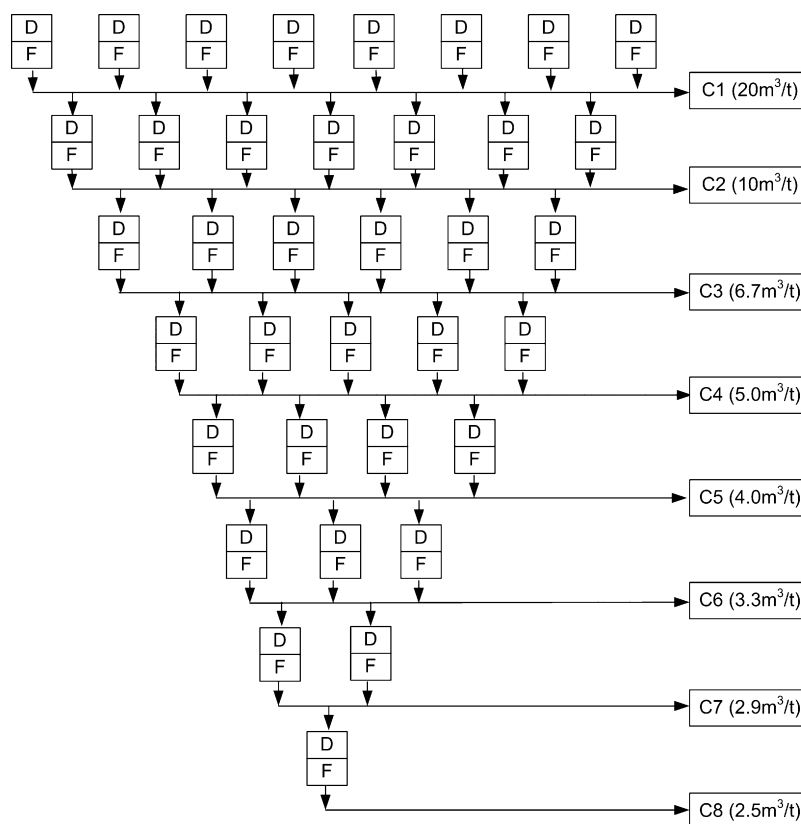


Fig. 1. Simulation of the accumulation of contaminants by successive disintegrations. Note: "D" indicates disintegration stage; "F" indicates Büchner filtration.

The release of contaminants from the recovered paper is calculated from several blocks (one for each specific contaminant) in which mathematical formulas are used. In the case of constant release, these functions are constant values. In the case of variable release of contaminants, the release equation curves obtained from lab-scale tests are used. The only necessary input is the concentration of the contaminant in the water circuits. The stream used for getting this value is the main flow just after the mixing tank. With these mathematical fits, the release of a contaminant in terms of ppm furnish is calculated in each one of the simulation steps. Maximum and minimum allowed values have been defined for these mathematical equations for avoiding problems in the convergence of the system. In the cases of fresh water consumptions in which the concentration for a specific contaminant is higher than the obtained during the lab-scale trials, the release is supposed to be constant and equal to the last value calculated.

3. Results and discussion

3.1. Influence of closure on DCM accumulation

Figs. 2–6 show the accumulation tendency for the different contaminants. It is observed that at high fresh water consumption (around 10–20 m³/t), the accumulation of contaminants is rather slow compared to the accumulation at low fresh water consumptions (especially < 5 m³/t). The best fit of the curves is a potential fit, drawn in the corresponding figures. Square coefficients of determination for these fits are higher than 0.97 for all the analyzed contaminants and for both types of papers, except in the case of alkalinity, in which square coefficients of determination are 0.80–0.90. First-order potential fits were also obtained by Heller et al. [26], using a pilot paper machine running continuously for

4 days under closed white water conditions. Other authors have obtained slightly different fits. Ravniak and Moze [27], for example, obtained hyperbolic fits, using a Rapid-Köthen lab sheet former for the simulation of the water loop closure.

In the present study, the accumulation of contaminants did not reach the steady state after eight recycling cycles. Other authors have also observed that steady state is not reached even with a high degree of closure, regardless of the methodology used for the simulation of the accumulation. Vendries and Pfromm [19], for example, simulated the closure of water circuits with a dynamic sheet former under acid rosin sizing conditions for producing linerboard from recycled paper. After 15 recycling cycles at a 100% level of closure, steady concentrations were not obtained for the analyzed

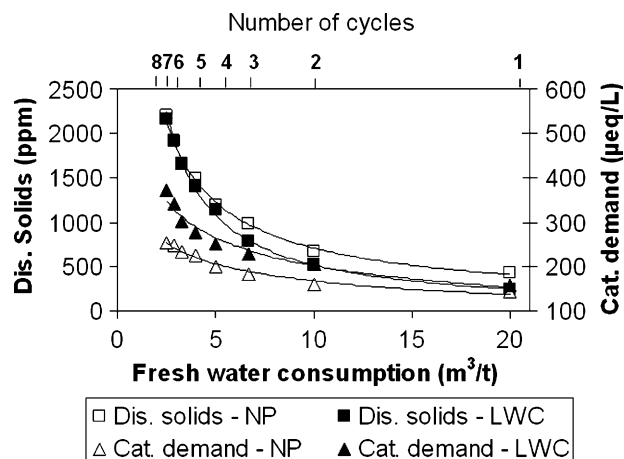


Fig. 2. Dissolved solids and cationic demand accumulation.

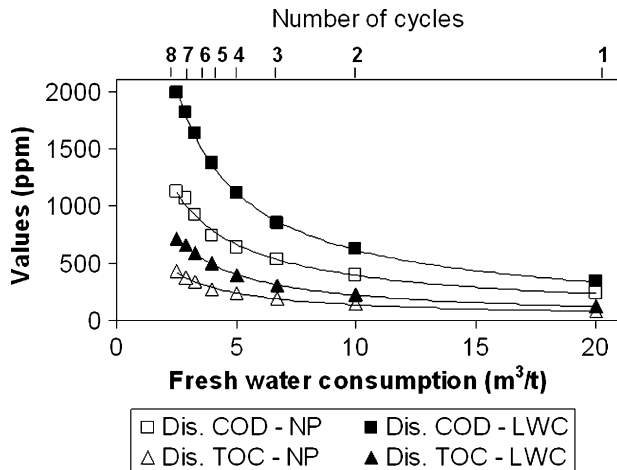


Fig. 3. Dissolved COD and TOC accumulation.

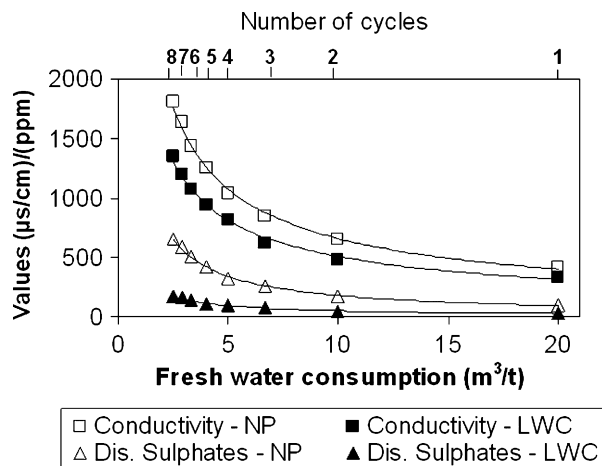


Fig. 4. Conductivity and dissolved sulphates accumulation.

contaminants (aluminium, sulphur, sodium and chloride). Xu and Deng [20], using a dynamic hand sheet former and reusing the waters after each cycle in the simulation of the closure of a liner-board mill, observed that the higher the recycle ratio, the longer the time required for reaching equilibrium; from experimental data, they performed a simulation in which the cycle numbers needed

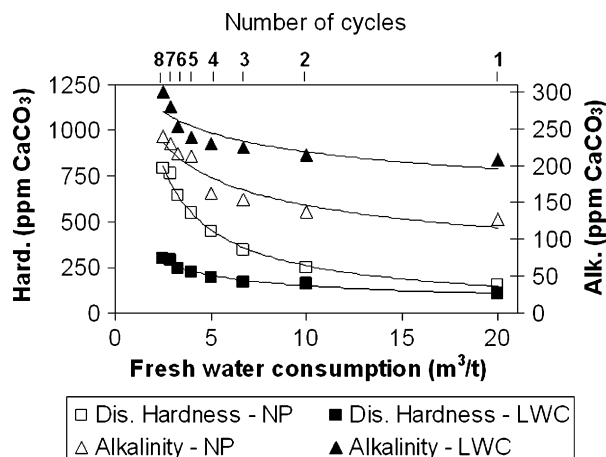


Fig. 5. Dissolved hardness and alkalinity accumulation.

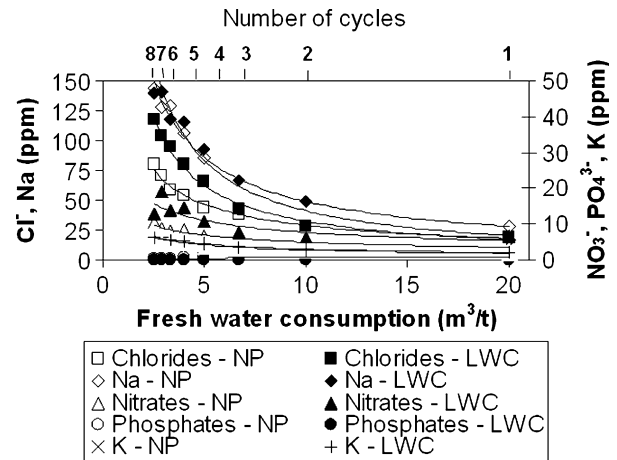


Fig. 6. Dissolved chlorides, nitrates, ortho-phosphates, Na and K accumulation.

to reach 99% of the final equilibrium concentration for sodium and calcium were 21, 29, 44 and 90, for recycle ratios of 0.80, 0.85, 0.90 and 0.95, respectively. Consequently, at least 100 cycles would be necessary for reaching the steady state if 100% level of closure is simulated, at least in terms of calcium and sodium. This could justify why in the study of Belosinschi and Bobu [22] the accumulation of DCM reached the equilibrium after only 6–7 cycles, because they used a relatively low level of closure (80%).

Although all the accumulation curves fit with first-order potential curves, fit parameters are very different for each specific contaminant, indicating different accumulation tendencies. For studying such a different behaviour, an accumulation factor (AF) has been defined for each specie, as the ratio between the final concentration of the contaminant after the recycling cycles (C8) minus its concentration in tap water (C0), and the concentration of the contaminant after the first cycle (C1) minus its concentration in tap water (C0) (Eq. (1)). This parameter indicates how fast the contaminant accumulates in the eight cycles. Theoretically, maximum value of accumulation factor in these conditions is 8. Related to the AF concept of the different species, Alexander and Dobbins [28] designated those species that had no affinity for the fibers and fillers as “non-substantive” while those that showed a high degree of adsorption on the fibers and fillers were called “substantive”. Consequently, as the water closure is tightened, substantive materials will leave the system with the fibers while the “non-substantive” species will remain in the recirculating water where they will accumulate. Contaminants with the highest AFs can be considered as non-substantive species, while contaminants with the lowest AF are substantive species. Table 1 shows the calculated AFs for the analyzed contaminants for both NP and LWC paper, except for dissolved Fe, Mn, Co, Zn and Cu (these metals were present only as traces in the waters).

$$(AF)_i = \frac{(C8)_i - (C0)_i}{(C1)_i - (C0)_i} \quad (1)$$

Organic material, measured by COD or TOC, presented a higher accumulation tendency ($AF \approx 5$) than inorganics, measured as conductivity ($AF \approx 4.2$). But specific salts, especially anions, have a low affinity for the fibers and are more prone to accumulate than other inorganic and organic species, e.g. sulphates. Monovalent ions such as sodium and chlorides have also a great tendency to accumulate. On the contrary, hardness and alkalinity are less prone to accumulate than the average of inorganics (conductivity). Total and dissolved solids accumulation is close to the average between organic material (COD and TOC) and inorganic material (conductivity). Accumulation of anionic trash, measured as cationic demand,

Table 1
AF values for the different contaminants.

Parameter	AF (NP)	AF (LWC)
Total solids	4.5	4.6
Dissolved solids	5.1	9.0
Cationic demand	1.8	2.4
Dissolved COD	4.8	5.8
Dissolved TOC	5.6	4.9
Conductivity	4.4	4.0
Dissolved sulphates	6.8	6.2
Alkalinity	1.9	1.4
Dissolved hardness	5.1	2.8
Dissolved chlorides	4.3	6.2
Dissolved nitrates	4.3	4.0
Dissolved orto-phosphates	3.6	4.0
Dissolved Ca	5.1	2.7
Dissolved Mg	4.1	2.8
Dissolved Na	5.1	8.5
Dissolved K	3.3	2.9
Dissolved Fe, Mn, Co, Zn, Cu	–	–

is lower than the accumulation of organics, indicating organic matter contributes only partially to the negative charge of the system. The same was observed by Zhang et al. [14] and Ravniak and Moze [27].

The results obtained are in accordance with the data published by Mittal et al. [21]. They developed a dissolved solid buildup curve for a North American linerboard mill with increased effluent recycling for different process configurations. In this study only inorganic compounds were measured. In all the studied cases, the maximum buildup was also obtained for sulphates followed by that of chlorides and sodium while low build-ups of calcium, magnesium and silica were observed.

As already mentioned, Vendries and Pfromm [19] investigated the buildup of some contaminants, mainly inorganics (conductivity, aluminium, sulphur, sodium, and chloride), and TOC, during the production of linerboard. In this case, six recycling cycles at a 100% level of closure were tested. From their data, the corresponding AFs were calculated. AF of the conductivity was 2.9 and 3.8 for TOC, indicating a higher accumulation of organic material compared to inorganic material. This is in accordance with the data obtained in the present work. Regarding the inorganic species, they obtained an AF of 4.2 for sulphur compounds, 3.4 for sodium and 2.5 for chlorides. The AF of aluminium was higher (7.0) because of the addition in each cycle of aluminium sulphate for sheet formation. In this study also sulphur compounds (mainly sulphates) are accumulated to a higher extent than monovalent cations and anions, such as sodium and chlorides.

Table 2
RF values for the different contaminants.

Parameter	RF (NP)	RF (LWC)
Total solids	2.4	1.7
Dissolved solids	1.5	1.0
Cationic demand	8.0	5.0
Dissolved COD	2.3	1.7
Dissolved TOC	1.9	1.8
Conductivity	2.4	2.2
Dissolved sulphates	1.2	1.1
Alkalinity	11.7	12.7
Dissolved hardness	1.8	4.2
Dissolved chlorides	1.6	1.1
Dissolved nitrates	2.4	2.3
Dissolved orto-phosphates	2.9	2.5
Dissolved Ca	1.6	2.6
Dissolved Mg	2.2	4.0
Dissolved Na	1.9	1.4
Dissolved K	2.9	3.7
Dissolved Fe, Mn, Co, Zn, Cu	–	–

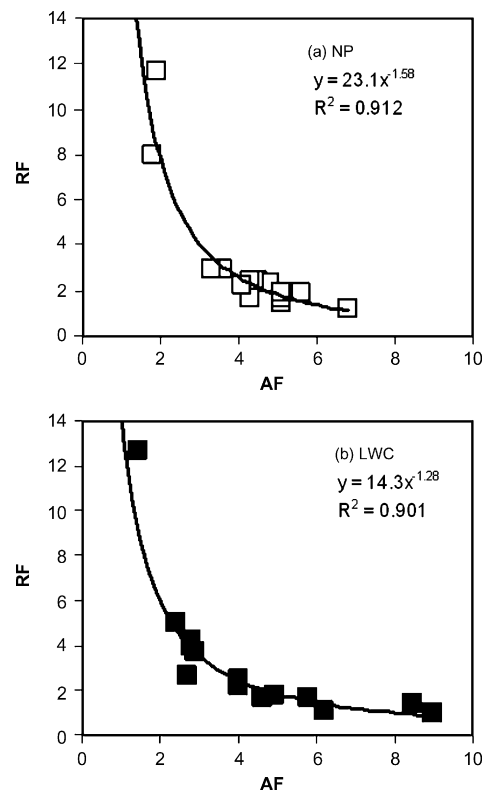


Fig. 7. RF versus AF for the different contaminants: (a) NP and (b) LWC.

In general, the contaminant load released from LWC paper has been higher compared to NP paper: the release of organics is between 40% and 80% higher (Fig. 3). However, the release of inorganics is in the major part of the cases higher in the case of NP paper compared to LWC paper, e.g. conductivity (25–35% higher), and especially in the cases of hardness (40–170% higher) and sulphates (nearly three times higher). Similar release of chlorides, nitrates, phosphates and metals were observed for both types of papers and only alkalinity was minor (20–40%) for NP than for LWC paper. General parameters as the total or dissolved solids or the cationic demand were very similar for both papers. Only minor differences have been observed in the trends, measured as their AFs, because the contribution of the raw material to the contaminant load release is the most important and the raw material used for producing NP and LWC paper is very similar. The same was observed by Ruiz et al. [29] comparing the release of contaminants in the disintegration of NP and two improved NP papers (supercalendered ones).

Higher organic content in LWC compared to NP paper can be easily explained by the presence of coating binders used in the paper coating, easily released during the pulping stage. Coating is used for enhancing the printing qualities and visual properties of the paper. This coating layer has a thickness of the order of 10 μm thick and can represent between 6 and 12 g/m^2 coating per side, meaning a 20% of the finished product [30]. A coating layer typically consists of (i) water, so that the coating can be applied as a particulate suspension; (ii) pigments, such as ground or precipitated calcium carbonates, clays, polymeric pigments (such as polystyrene), titanium dioxide, silica, or talc; and (iii) binders, which are needed to provide good cohesion of the porous structure formed by pigments and adhesion of this structure to the substrate. Binders are organics, either natural, such as starch or protein, or synthetic, such as styrene–butadiene, acrylic latex or poly(vinyl acetate)

Table 3
Release constant values and equations for the different contaminants used in the simulation of the process.

Parameter	Type of paper	Constant release (kg/t)	Range of application (ppm)	Variable release ^a kg/t = $aC_i^2 + bC_i + c$		
				<i>a</i>	<i>b</i>	<i>c</i>
Dissolved sulphates	NP	1.86	0–600	0	-3.28×10^{-4}	1.727
	LWC	0.46	0–160	0	-1.15×10^{-4}	0.449
Dissolved COD	NP	4.54	0–960	4.27×10^{-6}	-6.62×10^{-3}	4.589
	LWC	6.58	0–1790	4.90×10^{-7}	-2.27×10^{-3}	6.508
Dissolved TOC	NP	1.54	0–390	3.50×10^{-6}	-3.21×10^{-3}	1.548
	LWC	2.44	0–645	1.26×10^{-6}	-2.22×10^{-3}	2.360
Dissolved hardness	NP	2.61	0–790	1.03×10^{-6}	-1.95×10^{-3}	2.469
	LWC	1.67	0–305	1.58×10^{-6}	-1.00×10^{-2}	1.925

^a C_i : concentration of the contaminant, expressed in ppm (mg/L).

and can represent approximately a 10–20% (w/w) of the coating [31].

The higher amount of sulphates and hardness are the main responsible for the higher conductivity measured in NP compared to LWC. Sulphates and hardness are two of the most important inorganics in terms of concentration. In principle, LWC should release a higher content of sulphates than NP paper because the possible presence of gypsum as coating pigment in LWC. However, this is not the case. Dissolved hardness is also higher in NP higher than in LWC. This is probably a consequence of the lower pH of the waters obtained in the disintegration of NP compared to LWC. The dissolution of the main contributor to the hardness of the waters, calcium carbonate, is enhanced at lower pH [32], and differences of only 0.5 pH units can be very important in the

measured levels of dissolved hardness. Alkalinity in LWC paper is higher than in NP paper because of the coating pigments added to the paper and because the higher proportion of old magazines in the furnish, with a higher content of alkalinity sources than old newsprint.

3.2. Process simulation

Lab-scale tests have demonstrated clear differences in the accumulation behaviour for non-substantive and substantive species. On the other hand, results also indicate that the release of contaminants during pulping depends on the degree of contamination of the process water, especially in the case of substantive species. This release is higher at low contaminant load of the waters and lower at high contaminant load of the waters. In a similar

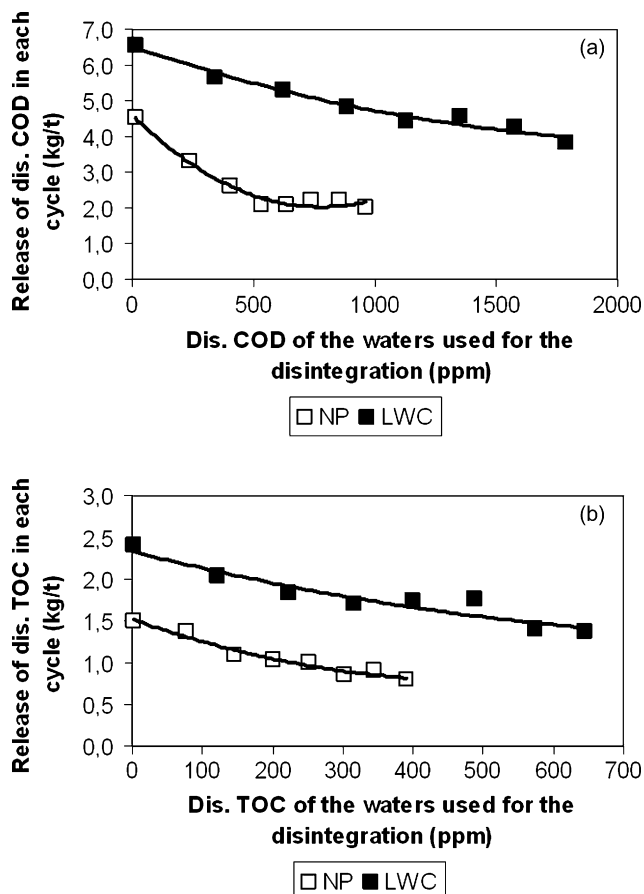


Fig. 8. Release curves of (a) dissolved COD and (b) dissolved TOC.

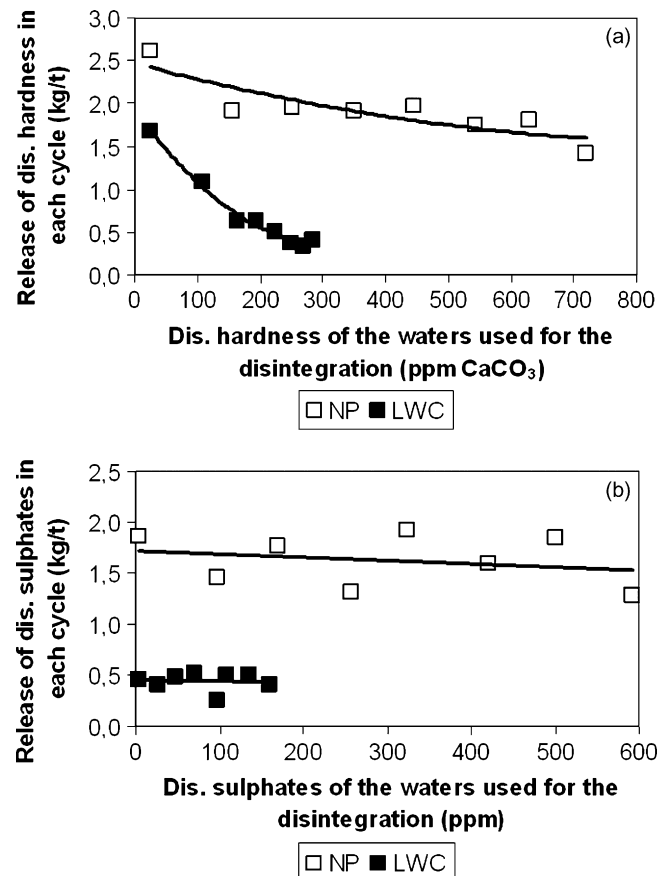


Fig. 9. Release curves of (a) dissolved hardness and (b) dissolved sulphates.

way in which AF was defined, a release factor has been defined as the ratio between the release of a contaminant in the 1st cycle (R1) and the release of the same contaminant during the 8th cycle (R8), both expressed as kg/t (Eq. (2)). In general, the release of a contaminant is obtained as the difference between the value of the concentration of the contaminant in cycle $i+1$ minus the value of the concentration of the contaminant in cycle i . This release is related to the amount of recovered paper in terms of kg/t, considering that in each of the cycles, 100 g of recycled paper is disintegrated in 2 L of water from the previous cycle.

$$(RF)_i = \frac{(R1)_i}{(R8)_i} \quad (2)$$

This parameter tries assessing the decrease in the release of the contaminants as a consequence of a higher contamination load of the waters. If RF is close to 1 it means that the release of the contaminant at a low level of contamination (1st cycle) and high level of contamination (8th cycle) is similar. If RF is higher than 1 it means that the release of contaminant in the 1st cycle is higher than in the 8th cycle, when the process waters have a higher degree of contamination. The higher the RF is, the higher the effect of the contamination of the process water on the release of contaminants is. Values of $RF < 1$ are also possible, although this is not common, this situation has occurred only for dissolved solids

of LWC paper and this value is close to 1 (0.96). RF values for the analytical parameters measured in this study are shown in Table 2.

According to their RFs, dissolved sulphates are the contaminants less affected by the contamination of the waters, its release is almost constant during the different recycling cycles. This is the predicted behaviour for typical non-substantive species. Chlorides and dissolved solids other contaminants with a close behaviour to sulphates. Organics (as COD and TOC) have a RF value of around 2, indicating that the release in the last cycle of accumulation is around a half of the release obtained in the first cycle. The release of inorganics, measured as conductivity, is slightly more affected by the contamination load of the waters ($RF \approx 2.2$). The major influence of the contamination load of the waters is in the cationic demand and alkalinity: the release in the last cycles can be as low as a 10% of the release in the first cycle.

A very clear relationship between the AF and the RF has been observed (Fig. 7). The AF indicates that the concentration of the contaminant in the process water in cycle 8 is n times higher than the concentration of the contaminant in cycle 1. But, in principle, this release can be similar in each of the cycles ($RF \approx 1$), or different. Non-substantive species have lower values of RF, close to 1, indicating that the release of these contaminants are not affected much by the level of contamination of the waters. In the case of substantive species, RF values are the highest

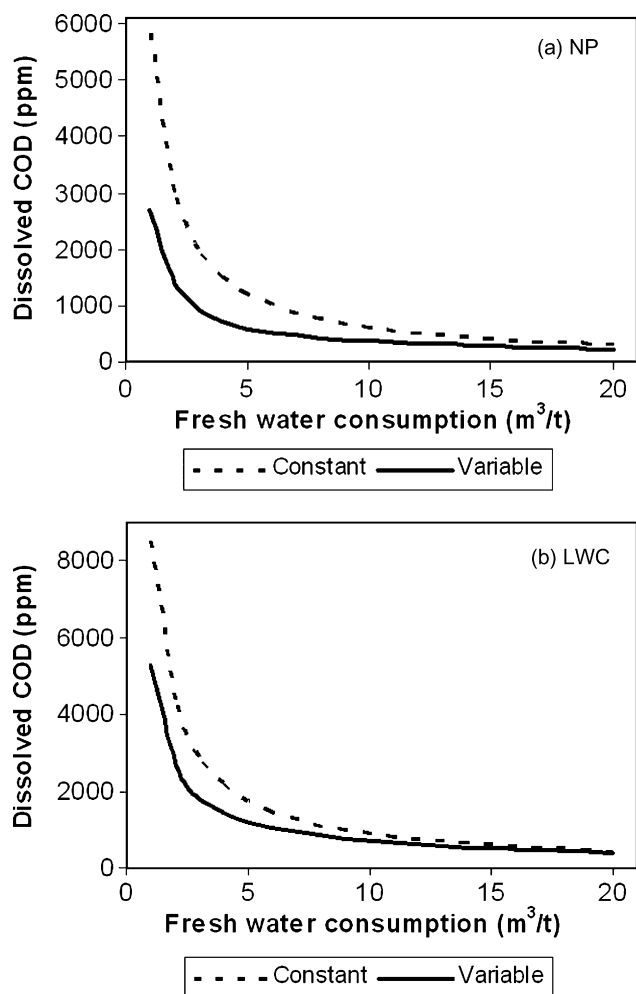


Fig. 10. Simulation of the accumulation of dissolved COD in process water versus fresh water consumption, using constant and variable release factors: (a) NP and (b) LWC.

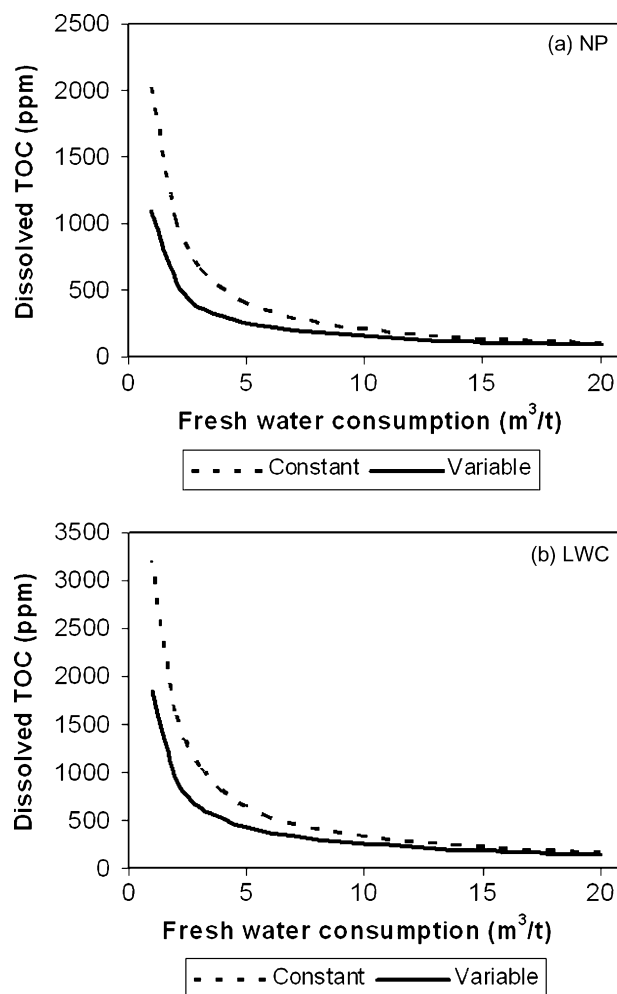


Fig. 11. Simulation of the accumulation of dissolved TOC in process water versus fresh water consumption, using constant and variable release factors: (a) NP and (b) LWC.

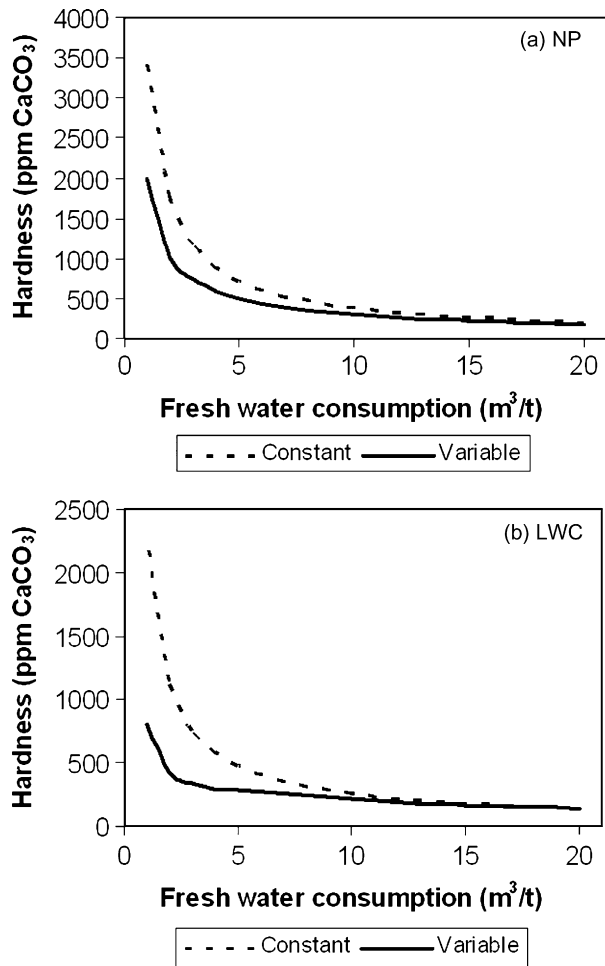


Fig. 12. Simulation of the accumulation of dissolved hardness in process water versus fresh water consumption, using constant and variable release factors: (a) NP and (b) LWC.

($RF > 8$ or $RF > 10$), indicating that the release of contaminants in the last cycles is very low compared to the release in the first cycle.

For the implementation of these observations in the simulation of the papermaking process it was necessary to fit the dependence of the release of a specific contaminant with the present concentration of this contaminant in the waters and obtaining the corresponding release curves. Figs. 8 and 9 show the release curves of four of the most significant parameters for determining the contamination load of waters: COD, TOC, hardness and sulphates.

In the case of dissolved COD, TOC or hardness, second-order polynomial fit was the best. In the case of non-substantive species such as sulphates, it has been observed that the release of these species is almost constant, independently of the contamination load, coefficient of determination for the linear fit of the data was as low as $R^2 < 0.07$, for both types of paper, indicating a negligible dependence of the release of sulphates with the concentration of sulphates in the waters. Table 3 shows the mathematical fits obtained and the application range of these release curves. It is also included the value of the release of the contaminant in the first cycle (R_1), which is used as the value for the constant release of contaminants to waters.

In the case of typical substantive species such as dissolved COD and dissolved TOC, with a RF between 1.7 and 2.3 (Figs. 10 and 11), differences are important even at the highest fresh water con-

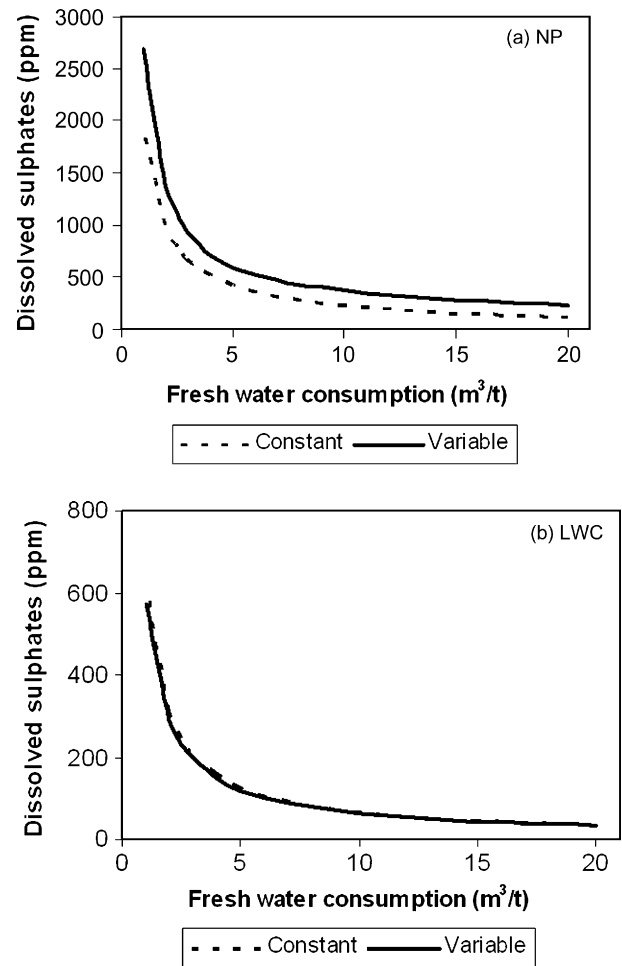


Fig. 13. Simulation of the accumulation of dissolved sulphates in process water versus fresh water consumption, using constant and variable release factors: (a) NP and (b) LWC.

sumptions. According to their similar RF values, the behaviour for dissolved COD and TOC was very similar. In the case of NP paper, the ratio between the dissolved COD obtained considering constant and variable releases ranged from 1.36 to 2.22 and from 1.18 to 1.85 in the case of dissolved TOC. For LWC paper, these ratios ranged from 1.15 to 1.64 and from 1.17 to 1.63, respectively. Similar results were obtained in the case of dissolved hardness (Fig. 12), with a ratio between values obtained at constant and variable release, ranging from 1.17 to 1.74 in the case of NP ($RF \approx 1.8$) and from 1.03 to 2.79 in the case of LWC paper ($RF \approx 4.2$).

As an example of the relatively low influence of using a variable instead of a constant release for non-substantive species, Fig. 13 shows the accumulation of sulphates in the water circuits as the fresh water consumption is reduced for NP paper ($RF \approx 1.1$ – 1.2). In the case of sulphates, differences between the values of dissolved sulphates assuming a constant release and variable release are the least of the studied cases, especially in the case of LWC paper (a maximum difference of a 7%). For NP paper, the maximum difference is 25%.

The main differences between assuming a constant or a variable release of a specific contaminant are found when the lowest fresh water consumptions are simulated (at the highest contamination load of the waters) and for the contaminants with the highest RFs. When simulating closed water circuits, the use of these types of release curves are strictly necessary because the real concentration of contaminants in the circuits can be two or three times

lower than expected, assuming a conventional constant release of contaminants.

4. Conclusions

Accumulation curves of a broad range of organic and inorganic contaminants in papermaking have been obtained. Steady state concentrations were not obtained after eight recycling cycles and a 100% level of closure. First-order polynomial fits described very well the accumulation curves in nearly all of the studied contaminants. Accumulation of contaminants was very different according to their affinity for the paper; accumulation of organic material (COD and TOC) is higher than inorganic material (conductivity) but some species such as sulphates or chlorides present a higher tendency to accumulate than organics.

The release of contaminants into process water is strongly dependent on the current degree of contamination of the waters, especially for substantive species. A very simple simulation of the papermaking process allowed the comparison of the influence of fresh water consumption on the concentration of the most common contaminants in water circuits considering the contribution of recovered paper both constant and variable (using the release curves obtained at lab-scale). It is clearly demonstrated that release curves obtained at lab-scale are necessary if accurate simulations of the process are required, especially in the simulation of relatively low fresh water consumptions or high contamination load in the circuits, in which the effect of not considering a constant release of contaminants is more important. It has been found that real concentrations of the contaminants can be two or three times lower than predicted if conventional constant release of contaminants is assumed.

The contaminant load released by LWC paper is higher in the case of organics (because the coating binders) and lower in the case of inorganics (because of differences in the manufacturing process and the used furnish), compared to NP. But only minor differences have been observed in the trends (AF and RF values) because the raw material used for producing NP and LWC is very similar and the contribution of the raw material is the most critical to the release of the contaminants.

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