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Determination of toxic compounds in paper-recycling process waters by gas chromatography–mass spectrometry and liquid chromatography–mass spectrometry

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Abstract

Three analytical methods were developed for the determination of toxic compounds in recirculating waters of a paper-recycling industry. Three main groups of compounds were considered: (i) wood extractives originated from the raw material; (ii) biocides added during the production process and (iii) surfactants and other adjuvants present in the formulates of these biocides. Wood extractives considered in this study included fatty and resin acids. They were analysed by liquid–liquid extraction using methyl *tert*.-butyl ether, followed by gas chromatography–mass spectrometry for previous formation of the respective trimethylsilyl esters. Water samples were also extracted with Oasis HLB (copolymer [poly(divinylbenzene-co-*N*-vinylpyrrolidone]) solid-phase extraction cartridges of 60 mg and analysed by liquid chromatography–electrospray mass spectrometry for the determination of additives and biocides. Using these two approaches levels up to 15 mg/l for total resin and fatty acids, 5 mg/l for alkylbenzene sulfonates and 2-(thiocyanomethylthio)benzotiazol, 100 μg/l for bisphenol A and 2,2-dibromo-3-nitrilepropionamide, and 300 μg/l for nonylphenol ethoxycarboxylate were detected in process waters at different production treatment stages. These levels are of relevance since poor water quality affects the paper-recycling process, the primary water treatment process and eventually, the environmental water quality.
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1. Introduction

Effluents and recirculating waters from paper-recycling industries are complex matrices containing large numbers of compounds of extremely high diversity, some of them presenting also high toxicity levels and conferring unpleasant smells in the surroundings. These compounds come basically from either the raw material (wood extractives) or from additives used in the paper production process (surfactants, bleaching agents, glues or biocides). Wood extractives dissolve or disperse in process waters during recycling and are, to a large extent, carried over to the paper machine. Particularly in paper industries with a high degree of white-water system closure, wood extractives can have a negative impact on paper machine and product quality (formation of pitch depositions on the paper machine, specks in the paper, etc.) [1,2]. An additional problem is that extractives and additives used in the

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production process can accumulate in the white-water system and finally end up in the process effluent or remain in the final product.

To face these problems a first step is a deep characterisation of process-water samples with the identification and determination of the major organic components that might affect paper quality or contribute to the water toxicity. The present work will be basically focused on the second aspect. To carry out the study, recirculating waters from a paper-recycling industry (Riudesa, St. Pere de Riudebitles, Catalonia, Spain) with total organic carbon (TOC) values up to 5000 mg C/l will be analysed using different methods.

Among wood extractives, resin acids are tricyclic diterpenoids, which occur naturally in conifers. They contain a very stable common carbon skeleton and are very resistant to chemical degradation, surviving the pulping and bleaching process. Resin acids and, to a smaller extent, the unsaturated fatty acids have been identified as the major contributors to the toxicity of effluents to fish. The 96-h LC_{50} values for salmon or rainbow trout are from 0.4 to 1.7 mg/l for the common resin acids and from 2.0 to 8.0 mg/l for fatty acids, which are similar to those of chlorinated guaiacols and catechols [3].

On the other hand, for the treatment of closed-water circuits, the addition of high amounts of biocides is required to decrease the problems related to microbial growth. The paper-recycling industry involved in the present work adds formulates containing 20% (p/p) of 2,2-dibromo-3-nitrile-propionamide (DBNPA) and 10% (p/p) of 2-(thiocyanomethylthio)benzotiazole (TCMTB) at rates of 17.1 and 3.6 l/day, respectively. Surfactants and other adjuvants are also present in these formulates and, therefore, indirectly added to the waters. Among them, the most relevant are bisphenol A (BPA) that is a common constituent of some plastics, linear alkylbenzenesulfonates (LASs), and degradation products of nonionic surfactants of alkylphenols (APEOs) such as nonylphenol ethoxycarboxylates (NPECs), 4-nonylphenol (NP), octylphenol ethoxycarboxylates (OPECs) and 4-octylphenol (OP). Fürhacker et al. [4] showed that the paper industry was one of the major bisphenol A contributors to the influent of a wastewater treatment plant. Moreover, high concentrations of NPECs (up to 1300 μg/l) were found in a group of paper mill effluents discharged to Fox River, WI, USA [5]. All these compounds are considered as endocrine-disrupting compounds that at low μg/l concentrations may potentially alter the normal hormone function and physiological status of animals [6,7]. Concretely, NP is well known for its endocrine disrupting effects and has been included as a priority pollutant in the New Framework Water Directive 2000/60/EC.

Therefore, it is of considerable interest to characterise process-water samples of paper mills in relation to these families of toxic compounds in order to reduce their levels in effluents and implement effective water treatment systems. Due to the contrasting nature of these compounds, this objective is achieved by the application of several methodologies in this work. Thus, resin and fatty acids were analysed by gas chromatography–mass spectrometry (GC–MS) of their trimethylsilylester derivatives, whereas the rest of the compounds were determined by liquid chromatography–mass spectrometry (LC–MS) using two different methods for additives and biocides. Quality parameters of the different methods were evaluated for the identified species. The optimised methodology was applied to water samples collected at different points of the closed-water circuit at the paper-recycling industry, where a primary treatment plant is installed.

2. Experimental

2.1. Standards and chemicals

All standards and chemicals used were of the highest purity commercially available. All resin acids were obtained with a purity between 90 and 99% from Helix Biotechnologies (Vancouver, Canada). They were all used without further purification. Fatty acids were supplied by Fluka (Buchs, Switzerland) with a purity >99%.

High-purity standards of OP and BPA were supplied by Aldrich (Milwaukee, WI, USA). Standards of NP and nonylphenol ethoxycarboxylate (NP_1EC) were kindly supplied by AGBAR (Aigües de Barcelona, Spain). Commercial LASs were supplied by Petroquimica Española in a single standard mixture with the proportional composition of the different homologues (C_{10}, 3.9%; C_{11}, 37.4%; C_{12}, 35.4%;

C_{13}, 23.1%). Heptylphenol (Aldrich) was used for the evaluation of matrix effects.

DBNPA was purchased from Frinton (Vineland, USA) with a purity of 99% and TCMTB from Dr. Ehrenstorfer (Augsburg, Germany) at a concentration of 10 ± 0.05 ng/μl.

HPLC-grade water, acetonitrile, methanol, dichloromethane, bis(trimethylsilyl)trifluoroacetamide (BSTFA), and trimethylchlorosilane were obtained from Merck (Darmstadt, Germany) and methyl *tert.*-butylether (MTBE) from Fluka. Analytical reagent grade acetic acid was from Panreac (Barcelona, Spain). The ion-pair reagent used was triethylamine (TEA) purchased from Sigma (St. Louis, MO).

2.2. Samples

Samples from five representative sampling points of the closed-water circuit, with the following locations, were collected.

1. Well water used by the industry for supplying fresh water.
2. Water coming out from the paper machine (exit process water).
3. Water entering the purifying plant system.
4. Water coming out from a 30 μm filter located after the purifying plant system.
5. Water from a small river close to the industry.

Samples were kept at 4 °C in the dark until analysis. Table 1 shows the results obtained in a preliminary characterisation of the water samples. The TOC value was determined using the US Environmental Protection Agency (EPA) 9060A method.

2.3. Analysis of resin and fatty acids

2.3.1. Liquid–liquid extraction and derivatization

A method adapted from the literature was used for the extraction and derivatization of resin and fatty acids [8]. Before extraction, water samples were centrifuged at 500 *g* for 20 min to remove fibres and particles. An aliquot of 4 ml of the supernatant was measured in a screw-capped test tube for liquid–liquid extraction. No pH adjustment was performed, since the pH values of samples were between 6 and 8, which are suitable values for an efficient extraction of fatty and resin acids [3,9]. A 2 ml volume of MTBE containing 10 μg of heneicosanoic acid (C_{21}) was added in the first extraction. C_{21} was used as internal standard (I.S.), since it was not present in paper-recycling waters and did not coelute with the other species. The sample was vigorously shaken by hand for 2 min and centrifuged at 300 *g* for 5 min. The clear MTBE layer was carefully pipetted off. The extraction was repeated twice with 2-ml portions of MTBE (free of I.S.). The combined MTBE extracts were evaporated with a Reacti-Vap3 (Pierce) operating under a gentle stream of nitrogen to dryness. For derivatization, 80 μl of BSTFA and 40 μl of trimethylchlorosilane were added to the residue of evaporation. The solution was kept in an oven at 70 °C for 20 min and was thereafter ready for analysis.

2.3.2. Gas chromatography–mass spectrometry

A Trace GC–MS instrument (Thermoquest) equipped with a HP-5MS column (30 m×0.25 mm I.D. with 0.25 μm film thickness) containing 5% phenyl–methylsiloxane (model HP 19091S-433) was used. The oven temperature was held at 120 °C for 2 min and programmed to 300 °C at a rate of 4 °C/min. The final temperature was held for another 5 min. The inlet, ion source, and GC interface temperatures were 260, 200, and 270 °C, respectively. The carrier gas was helium at 10 p.s.i. (1 p.s.i.= 6894.76 Pa). The mass spectrometer was operated in the electron impact ionisation mode with an ionising energy of 70 eV and an emission current of 150 μA. All injections were done in the splitless mode and 1

Table 1
Some characteristics of water samples

Sample	TOC (mg/l)	pH	Conductivity (mS)
(1) Well	172	7.5	1.34
(2) Exit process water	5560	6.4	8.45
(3) Entrance purifying plant system	4905	6.2	9.92
(4) Exit filter	4905	6.5	8.46
(5) River	209	8.2	0.98

μl of the sample was injected. Full scan data were obtained by scanning from m/z 45 to 600 at a rate of 1.5 scans/s.

2.4. Analysis of additives and biocides

2.4.1. Solid phase extraction

Since waters from the paper industry contained a very high TOC value, and fibres and starch were present in all types of samples studied, waters had to be filtered through 1, 0.7 and 0.45 μm glassfibre filters (Whatman, USA). Only the dissolved fraction was analysed. Preconcentration was achieved using disposable Oasis HLB copolymer [poly(divinylbenzene-co-*N*-vinylpyrrolidone] SPE cartridges of 60 mg (Waters, Milford, MA, USA). Cartridges were conditioned with 8 ml of methanol and 5 ml of HPLC water. A 200-ml volume of water was percolated through the cartridge at a flow-rate of 6 ml/min using a Baker SPE 12g apparatus (J.T. Baker, Deventer, The Netherlands). Afterwards, cartridges were rinsed with 1 ml of HPLC water to remove matrix interferences. Cartridges were dried under vacuum for 20 min to remove the water and immediately after were eluted with 10 ml of methanol–dichloromethane (9:1, v/v). These extracts were evaporated to dryness with a Reacti-Vap3 (Pierce) operating under a gentle stream of nitrogen and reconstituted with methanol to a final volume of 1 ml.

2.4.2. Liquid chromatography–mass spectrometry

The HPLC system consisted of a HP1100 autosampler and a HP 1090A LC pump both from Hewlett-Packard (Palo Alto, CA). Chromatographic separation was done using a LiChrospher 100 RP-18 reversed-phase C_{18} analytical column (250×4 mm, 5 μm particle size) preceded by a guard column (4×4 mm, 5 μm) of the same packing material from Merck. Detection was carried out with an MSD HP 1100 mass-selective detector equipped with an electrospray ionization (ESI) interface and a single quadrupole analyser.

For the analysis of surfactants and BPA, the LC–ESI–MS was operated in the negative mode and a gradient elution with two solvents was used: (A) acetonitrile–water (8:2) and (B) water, both containing 0.05% acetic acid and 0.05% TEA. The elution gradient started with 30% A, kept isocratic 5 min, and linearly increased to 100% A in 15 min, a condition that was kept isocratic for 15 min.

For the analysis of biocides, LC–ESI–MS was operated in the positive mode and a gradient elution with two solvents was also used: (A) acetonitrile and (B) water, both containing 0.1% formic acid. The elution gradient started with 30% A, linearly increased to 50% A in 5 min, and linearly increased to 75% A in 10 min, a condition that was kept isocratic for 5 min.

Operating parameters of the MS system were optimised in the full-scan mode (m/z values, 50–500) by flow injection analysis (FIA). Final conditions were as follows: drying gas (N_2) at a flow of 12 l/min and a temperature of 325 °C, nebulizer pressure of 55 p.s.i., and capillary and fragmentation voltages of 3500 and 80 V, respectively. In both cases the flow-rate was 1 ml/min and 20 μl of the sample were injected for each analysis.

3. Results and discussion

A preliminary characterisation of the process water samples (Table 1) showed, apart from high conductivities, extremely high TOC values. This suggested that water samples were very charged with organic compounds, which might be attributed to the paper-making process where large amounts of additives and starch are used during manufacturing. Moreover, the TOC did not vary despite the water treatment used, indicating a poor efficiency of the purifying plant system, which consists of a single primary treatment.

As mentioned before, various families of compounds were candidates for analysis in this study: resin and fatty acids, biocides, and surfactants and other adjuvants present in the formulates of biocides. From each family, the most common species were checked. The structures of these compounds are shown in Fig. 1. The overall scheme of the analytical procedures used for the characterisation of process waters is shown in Fig. 2, and is especially suitable to analyse the different families of compounds, covering various polarities.

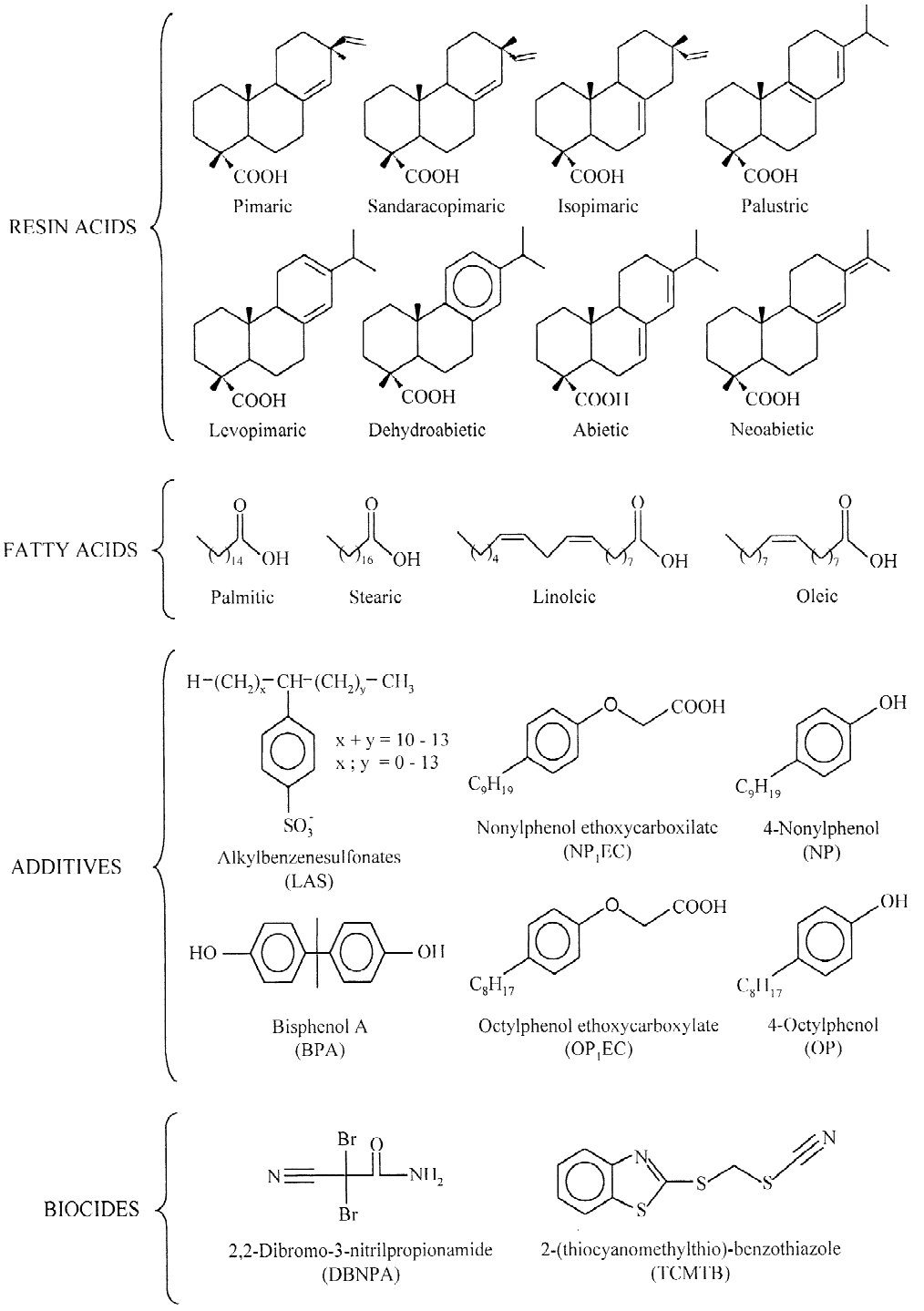

Fig. 1. Structures of target compounds to be detected in process-water samples.

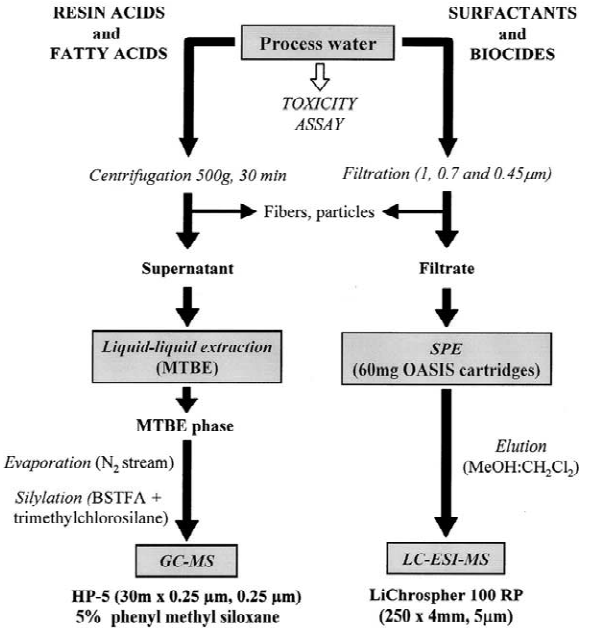

Fig. 2. Flow diagram of the analytical methods used.

3.1. Analysis of resin and fatty acids

The identification of the target compounds was done in the full-scan mode by matching the retention time and mass spectrum with authentic standards. Three ions were monitored for each compound to ensure their identification. Table 2 shows the monitored ions as well as the retention times for a resin acid (DHA) and three fatty acids (palmitic, oleic and stearic), the only compounds found in the water samples. Fig. 3 shows the total ion current (TIC) chromatograms of a process water sample and a mixture of the standards of the identified compounds. Because of the similarity among fatty acids, common m/z peaks were observed for the three compounds, mostly related with the trimethylsilylated (TMS) carboxylic group. Thus, all of them presented highly intense peaks corresponding to $[TMS]^+$ (m/z 73), $[COOTMS]^+$ (m/z 117), $[CH_2–COOTMS]^+$ (m/z 131) and $[CH_2–CH_2–COOTMS]^+$ (m/z 145), the most selective ions for each compound corresponding to the less intense $[M]^{+\cdot}$ and $[M-15]^{+\cdot}$ (loss of a methyl group). DHA also presented the same fragmentation, with the difference that the base peak appeared at m/z 239, corresponding to $[M]^{+\cdot}$ with losses of COOTMS and CH_3 groups.

Quantification of target compounds was performed using single ion monitoring (SIM). To choose the most suitable ions, preference was given to the most selective peaks for each compound, and the criterion of intensity was placed in second place. Thus, the peak corresponding to m/z of $[M-15]^{+\cdot}$ allowed a better discrimination among compounds than the base peak, sensitivity being still suitable for quantification. Table 2 shows the relative abundance of this ion for each compound. This choice was important to avoid interferences, particularly in the case of fatty acids, which have very intense peaks at low m/z values, common to many compounds with long hydrocarbon moieties.

Quality parameters of the method were determined only for the identified species. Series of injections of the standards in the range from 5 to 100 ng were used to obtain the calibration curves (peak area vs. mass injected, both relative to the I.S.). Good correlations were obtained with $r^2>0.99$. Because of the use of different ions for the quantification of the four compounds, response factors (RFs) with respect to the internal standard were considerably different from unity. As shown in Table 3, they were within a factor of three among compounds, with the stearic

Table 2
Retention times and monitored ions of the fatty and resin acids detected in process waters

Compound	Retention time (min)	Monitored ions (m/z)		
		Base peak	$M^{+\cdot}-15$[a]	$M^{+\cdot}$
Palmitic acid	23.03±0.05	117	314 (80)	328
Oleic acid	26.78±0.03	117	339 (75)	354
Stearic acid	27.38±0.06	117	341 (80)	356
DHA	30.33±0.05	239	357 (20)	372
Heneicosanoic acid (I.S.)	33.35±0.02	117	383 (75)	398

[a] Ion used for quantification. Relative abundance (%) in parentheses.

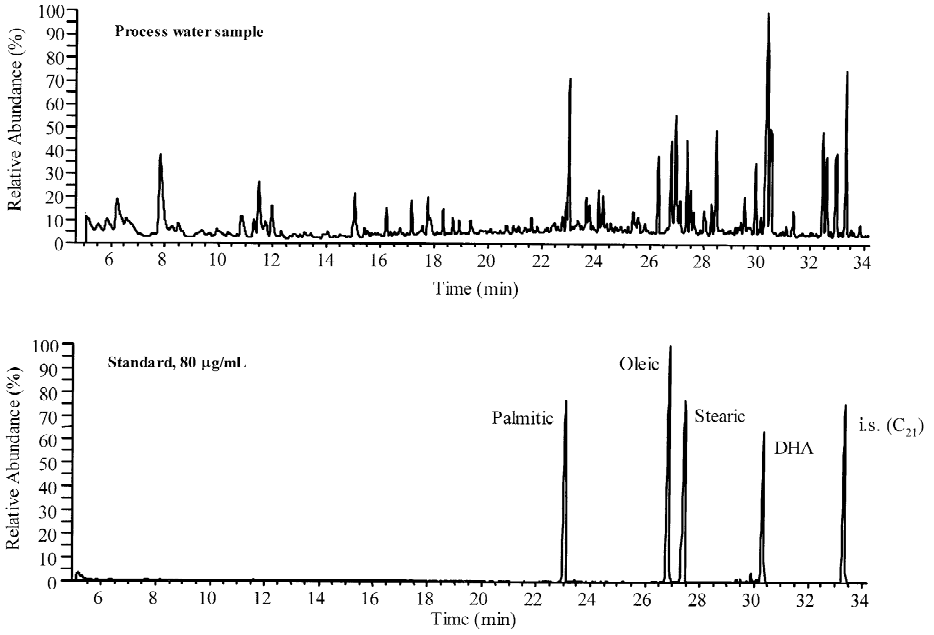

Fig. 3. Full-scan GC–MS chromatograms of a process-water sample (exit process water, sampling point 2) and a mixture of the standards of the resin and fatty acids.

and the DHA being the most and the least responsive compounds, respectively.

The recoveries of fatty and resin acids were obtained by analyses of fortified tap water samples ($n=4$) at levels close to those of real process-water samples (2.5 mg/l). As shown in Table 3, similar recoveries were obtained for all the species ranging from 60 to 80% with acceptable relative standard deviations (RSDs). The use of internal standard is, thus, necessary for the quantification of these compounds. Table 3 shows the instrumental detection limits (LOD_{inst}), as well as method detection limits (LOD_{method}) using process water samples, this later being corrected by the percentage of recovery. In both cases, a signal-to-noise ratio ≥ 3 was considered. Method detection limits were at the low μg/l level, easily attaining the purpose of monitoring fatty and resin acids in paper-recycling waters.

3.2. Analysis of additives and biocides

Additives and biocides were analysed using an ESI interface. Whereas surfactants and BPA were detectable in negative ion mode [10], positive ion mode was required to determine biocides [11].

The use of ESI provided a high level of specificity and sensitivity for BPA and degradation products of nonionic surfactants of alkylphenols (APEOs) such as NP_1EC, NP, OP_1EC and OP (see structures in Fig. 1). Single ion monitoring of the molecular ions

Table 3
Quality parameters for the determination of the identified fatty and resin acids

Acid	RF	% Recovery (RSD, %, $n=4$)	LOD_{inst} (pg injected)	LOD_{method} (μg/l water)
Palmitic	1.0	71 (6)	17	3
Oleic	0.7	61 (4)	20	3
Stearic	1.3	79 (6)	9	5
DHA	0.3	75 (9)	43	9

$[M-H]^-$ at m/z 227 (BPA), 263 (OP_1EC), 277 (NP_1EC), 219 (NP), and 205 (OP) was employed for the determination of these species. Under the chromatographic conditions used, LASs were also determined. They co-eluted with the surfactant species, but were unequivocally identified by the corresponding retention time, their molecular ions at m/z 297 (C_{10}LAS), 311 (C_{11}LAS), 325 (C_{12}LAS), and 339 (C_{13}LAS), and a confirmation ion at m/z 183. Quantification was performed using the respective molecular ions. Fig. 4 shows the TIC chromatogram of a process-water sample as well as the SIM chromatograms of the respective analysed compounds. Due to the complexity of the matrix, extracts often showed systematic peaks but they did not interfere with the identification of the compounds of interest.

Recoveries for additives and biocides were determined by fortification of tap water ($n=3$) and they were higher than 90% for all the species. Matrix effects were discarded after comparing the recovery of a spiked water extract with heptylphenol at 1 μg/ml with a heptylphenol standard at the same concentration. A series of injections of the standards in the range from 1 to 150 μg/ml for BPA and NP_1EC, from 1 to 10 μg/ml for C_{10}LAS, and from 10 to 50 μg/ml for the rest of LAS were used to obtain the calibration curves, with $r^2>0.99$ in all cases. Detection limits (signal-to-noise ≥ 3) were variable depending on the species, ranging from 0.5 μg/l for BPA to 10–80 ng/ml for NP_1EC and LAS.

The two biocides, TCMTB and DBNPA, were analysed under the same chromatographic conditions. The use of ESI interface with detection in the positive ion mode was considered the most suitable for the identification and determination of these two species. For the benzotiazole (TCMTB), two main fragments at m/z 180 and 136 were identified that corresponded to losses of a −HSCN fragment and an additional −CS fragment, respectively. This fragmentation was already suggested by Ferrer and Barcelo [12]. The first peak was used for quantification and the second for confirmation.

For DBNPA, only a significant peak at m/z 182 was observed, which was used for the quantification of samples. No confirmation by other peaks was possible, but a peak with identical mass spectra and retention time as that of the standard was obtained in the water samples ensuring the presence of DBNPA. The TIC chromatograms of a process-water sample are shown in Fig. 5 together with the TIC chromatograms of the two individual standards.

Reliable calibrations were obtained with concentrations ranging from 0.05 to 5 μg/ml for TCMTB and from 15 to 85 μg/ml for DBNPA, with coefficients of correlation exceeding 0.999 in both

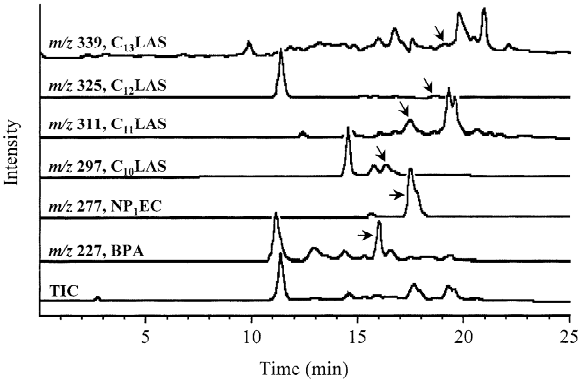

Fig. 4. LC–ESI–MS chromatograms (TIC) of a process-water sample (exit process water, sampling point 2) and SIM chromatograms of the respective analysed surfactants and BPA. The arrow appearing in each SIM chromatogram indicates the peak of the corresponding compound. LAS, linear alkylbenzenesulfonates; NP_1EC, nonylphenol ethoxycarboxylate; BPA, bisphenol A.

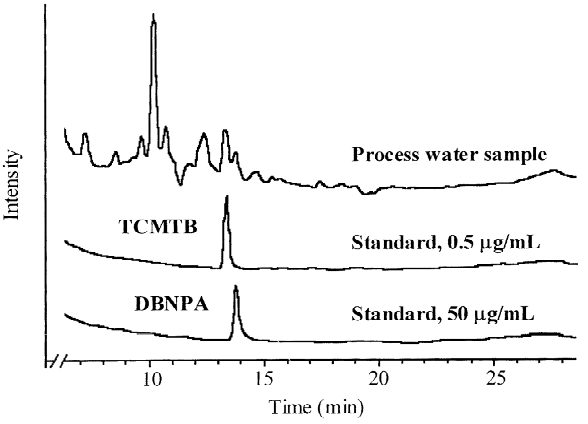

Fig. 5. LC–ESI–MS chromatograms (TIC) of a process-water sample (exit process water, sampling point 2) as well as of the individual standards of biocides.

cases. Detection limits of 1.5 μg/l for TCMTB and 80 μg/l for DBNPA were found considering a signal-to-noise ratio ≥3.

3.3. Concentration of toxic compounds

In a previous step, the toxicity of the paper-recycling process waters was measured by bioluminescence inhibition assays using the method developed by Farré et al. [13]. Bioluminescence inhibition values were around 100% for the process-water samples, indicating the presence of considerable amounts of toxic species.

Table 4 includes an inventory of the identified compounds in the process waters of the various sampling points, as well as their concentrations. Total resin and fatty acids were found at levels up to 6 and 8 mg/l, respectively, which agree with literature data for non-treated process waters [8,14,15]. These levels are of high relevance considering that the 96-h LC_{50} values for fish are from 0.4 to 1.7 mg/l for the resin acids and from 2.0 to 8.0 mg/l for fatty acids. In general, concentrations found were lower for the well and river waters than for the process waters, although differences were moderated. Moreover, slightly lower concentration levels were observed in the process water at the exit of the 30 μm filter, indicating a certain effectiveness of this water filtration. Another aspect to highlight is that only a resin acid, DHA was identified in the waters analysed. This might be explained by the fact that those resin acids with conjugated double bonds can easily undergo isomerization forming thermodynamically more stable isomers, with dehydroabietic acid being the favoured final product [16,17]. For this reason, only the most persistent resin acid (DHA) was detected in the waters of the paper-recycling industry. This is a difference with industries that start from wood, since in this case most of the resin acids can be identified [3,15,17]. For fatty acids, three species were detected (palmitic, oleic and linoleic acids), which agree with those reported in the literature [3,15].

High concentrations of LASs with levels up to 5000 μg/l were detected. However, unlike the TOC values, the LAS concentrations decreased from 5000 to 2000 μg/l, indicating that some of them were eliminated during the treatment. An aspect to remark on is that considerable concentrations of LASs were found in the supposedly clean waters taken from the well and the river. Although Riudesa works in a closed-water circuit, other factories located upstream from it may freely release their effluents. LASs form the major surfactant class used in detergents, because of their effectiveness and environmental safety and, therefore, their presence in wells and river waters might be related to either paper or other industrial uses. BPA, suspected to migrate from the plastics, also showed 50% elimination after primary treatment. Levels of BPA found in this study ranged from 54 to 110 μg/l, which agree with those from Fuhacker et al. [4] for waste waters of paper production industries (28–72 μg/l). However, BPA was not found in well nor river water. For NP_1EC, this reduction in concentration was not observed, this compound persisting in water or even increasing in concentration along the treatment. This is attributed to the degradation of long-chain NPECs under

Table 4
Concentration of toxic compounds in the process water samples

Sample	Concentration (mg/l)				Concentration (μg/l)				
	Palmitic acid	Oleic acid	Stearic acid	DHA	LAS_{TOT}	BPA	NP_1EC	DBNPA	TCMTB
(1) Well	0.8	1.1	0.7	4.0	275	0.4	<LD	<LD	<LD
(2) Exit process water	1.8	1.0	1.2	5.4	5048	110	72	116	1.9
(3) Entrance depuration	4.2	0.7	3.4	6.3	2044	54	289	n.a.[a]	n.a.
(4) Exit filter	1.0	0.4	0.7	4.1	2319	74	190	8.5	3.9
(5) River	1.3	0.5	1.1	6.5	162	0.4	0.6	<LD	<LD

[a] n.a., not analysed.

abiotic conditions forming short-chain NP. For this compound concentration values were between 72 and 289 μg/l, which also agreed with those reported by Field and Reed [5] for paper mill effluents (2–140 μg/l). The rest of the APEO degradation products were not found in any of the waters analysed. The absence of NP was attributed to its high partitioning to the particulate matter of the sample, given the high octanol–water partition coefficient (K_{ow}) of this compound.

Biocides were only detected in process waters, indicating that significant concentrations of these compounds added during the process still remained in the water, especially for DBNPA. This was mainly attributed to the continuous input of these biocides during the production process. A problem related to the presence of these contaminants in the process waters is that due to their physico-chemical properties, they can accumulate in the final paper product. Therefore, doses should be reduced as far as possible to avoid these contamination problems. In addition, these levels are enough to inhibit bacterial growth in case of secondary treatment. Finally, it was observed that the relative concentration between DBNPA and TCMTB in the process waters agreed with the relative amount of the two biocides added during the production process. However, the values obtained indicated that DBNPA might persist longer in the water than TCMTB.

4. Conclusions

Paper-recycling waters showed high toxicity indexes, which might be basically explained by the high levels of toxic species found. Due to the complex composition of these waters, characterised with a TOC of 5000 mg C/l, several methods were optimised for the identification and quantification of a high diversity of compounds. Liquid–liquid extraction followed by GC–MS allowed the determination of palmitic, oleic, stearic and dehydroabietic acids, whereas SPE with LC–MS permitted the detection of bisphenol A, nonylphenol ethoxycarboxylate and various linear alkylbenzenesulfonates. All these compounds were detected in the closed-water circuit, and their concentration did not significantly vary before and after the primary treatment. In addition, although a paper-recycling plant uses old paper rather than pulp for their manufacturing, fatty and DHA acids were still encountered in the process waters, treated or not, indicating a large high life and persistence in these waters. The high TOC of well and river waters (normal value 5 mg C/l) was correlated by relatively high concentrations of all studied compounds, except biocides. This was attributed to upstream discharges of other industries, and possible lixiviation in the case of well water.

The overall results indicate that toxic compounds are present in paper-recycling industries at levels comparable to pulp and paper industry. Therefore, there is an emerging need to close the water circuit and implement secondary treatments to enhance water quality and avoid problems of odor in this type of industry.

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