INVESTIGATIONS ON THE BEHAVIOUR OF UNDESIRABLE CONSTITUENTS

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**ABSTRACT**

In this paper comparison of the amounts of different organic and inorganic substances in recycling papers manufactured in 1991 and in 2005 in Germany is described. To evaluate the accumulation of hydrophobic compounds in paper produced of 80 to 100 % recovered paper, 15 paper samples (Graphic paper, Tissue paper, Packaging paper) were investigated regarding their chemical constituents. The amount of halogenated organic compounds and other harmful organic and inorganic substances in the paper samples from 2005 are of a lower or equal level as 1991. An enrichment of undesirable constituents due to repeated recycling of fibres could not be stated.

**INTRODUCTION**

In Germany the recovered paper utilization rate has continuously increased in the past years. In 2006, 67 % of the utilized fibres were derived from recovered paper. Figure 1 shows the increase of recovered paper utilization rate in Germany for the sum of all paper grades [1].

![Figure 1: Development of recovered paper utilization rate in Germany in the last 10 years](image)

Because of the increasing closure of fibre and water cycle and the high number of recycling circuits it is suspected that the amount of substances with high fibre affinity, part of them harmful, will considerably increase in the current paper production if not discharged from the cycle. Many of the harmful and undesirable compounds are hydrophobic compounds. They will therefore not be discharged with the process water and thus will occur only in very small amounts in the effluent. In recovered paper processing other possibilities to reduce the amount of hydrophobic substances exist:

- the adsorption on the surface of the hydrophobic fines
- the accumulation in deinking sludges and fibre rejects.
Two strategies are applicable to avoid increasing the concentration of undesirable substances in paper-recycling cycle and the accumulation of harmful compounds in papers made from recycled fibres:

- minimizing the amount of harmful substances that are added to the cycle when manufacturing new paper
- improvement of discharge efficiency of the cleaning systems

Baumgarten and Großmann [2] developed static and dynamic models to describe the degree of accumulation of contaminants in recycled papers as a function of the recovered paper utilization rate. An exponential increase of the concentration of undesirable constituents is expected, as shown in Figure 2. Accordingly, accumulation of hydrophobic substances in papers should depend on the transfer coefficient for the component in question.

\[
\frac{\text{v} = \frac{a \cdot t_n}{1 + M - a \cdot t_n}}{\text{Parameter:}}
\]

\[
t_n = 0.95 \quad M = 0.2
\]

\[
t_n = 0.8
\]

\[
t_n = 0.6
\]

\[
t_n = 0.4
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\[
t_n = 0.2
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\[
t_n = 0.1
\]

\[
t_n = 0.05
\]

In the last years some prominent changes have influenced the production process and the accumulation or removal of undesirable constituents from the fibre cycle. These developments concern particularly:

- the manufacturing of virgin fibre pulps,
  (for example introduction of totally chlorine free (TCF) or elementary chlorine free bleaching (ECF) instead of chlorine bleaching processes for production of chemical pulps and more restricted use of complexing agents in mechanical pulp bleaching processes)

- the selection of chemical additives for paper manufacturing, paper finishing and paper converting in consideration of recyclability,

- the optimization of recovered paper processing
  (for example multi-stage flotation and/or wash deinking systems in paper mills which produce graphic or tissue papers) and

- the progressive closure of process water circuits with the possibility of accumulation of organic and inorganic constituents.
Most of the above mentioned factors act contrarily to the predicted enrichment of undesirable constituents in recycling papers. A quantification of these influences is difficult. It appears therefore reasonable to consider the mathematical models with measurements of harmful substances in papers made from recovered paper. The German paper industry has provided a basis for this empiric approach by funding a research project in 1991 carried out by the former Institut für Papierfabrikation of the Technische Universität Darmstadt. The content of this project was the investigation of 25 representative paper samples from recovered paper processing mills in Germany regarding their amount of harmful substances [3].

**OBJECTIVE**

The target of the investigations in 2005 was to repeat the analyses of paper and board from the same paper mills which were investigated in 1991. Samples from the production process were analysed to compare the concentration of harmful substances in paper and board between 1991 and 2005. The results should be the base for the assessment of the accumulation of hydrophobic or hydrophilic substances in paper and board made from recovered paper in 2005 (recovered paper utilization rate of 66 %) compared with 1991 (recovered paper utilization rate of 49 %). The following assumptions for the sampling were fixed:

- The paper mill should produce the same or nearly the same paper grade in 2005 as in 1991.
- The grade of recovered paper as the most important raw material should not differ between 1991 and 2005.
- The recovered paper processes should be comparable in the two spaces of time.
- The white water circuit and the white water management should not be very different in 1991 and 2005.

**SAMPLING AND ANALYSES**

Considering the above mentioned assumptions, 15 of 25 paper mills complied with the requirements given above. The paper samples were taken daily directly at the reel drum by the paper mill on 10 consecutive days, wrapped in aluminium foil and sent to the laboratory of PMV, Technische Universität Darmstadt. In the laboratory a mixed sample was made from the 10 daily samples. A questionnaire about raw materials, chemical additives, fresh water consumption, waste water discharge, white water circuit and manufactured paper grade was filled in by the mill staff.

Along the lines of the investigations in 1991 the following parameters have been investigated:

- **Inorganic constituents**
  - Borate, bromide, chloride, fluoride, nitrate, phosphate, sulphate, nickel

- **Organic constituents**
  - Halogenated organic components, water soluble halogenated organic components, pentachlorophenol (PCP), polychlorinated biphenyls (PCB), primary aromatic amines, formaldehyde, phthalates

- **Other parameters**
  - Substances for microbiological control, optical brighteners (OBA), dye stuff constituents

Because of the current discussion in Germany about polycyclic aromatic hydrocarbons (PAH) and diisopropylnaphthalene (DIPN) analyses of these components were added to the investigation. These parameters have been analysed in the current samples from 2005 as well as in the retained samples from 1991.

The steps for the sample preparation are shown in Figure 3.
Figure 3: Procedure of sample preparation

For each constituent, the chemical analyses were carried out in consideration of the present standardized test methods; directly in the paper sample, in the cold water extract of the paper sample or after the extraction with a suitable organic solvent (see Figure 4).

Figure 4: Analytical parameters and sample preparation

For the procedure of chemical analysis, the steps of sample preparation and the analytical conditions were of great importance to get comparable results for the amounts of organic and inorganic compounds in 1991 and 2005.
Therefore all processes of the analytical methods were carried out in 2005 in the same way as 1991 although for single parameters the standardized tests methods were modified in the time lap. For instance the quantitative analyses of PCP were carried out in a methanol extract in 1991 but the current test method allows the determination in a cold water extract.

RESULTS

Inorganic constituents

Borates

Borates are the salts of boric acids. The most important and widely used borate is Borax (Sodium tetra borate). Borax is used in the glass, enamel and porcelain industry but also to manufacture washing agents and fertilizers. The paper industry uses boron compounds in paper manufacturing and paper processing. Borates are expanding agents for common additives like starch, casein and animal glue and it has preservative effects. Furthermore, borates are effective agents for rheologic stabilisation of starches. This property is used in the starch glue processes of corrugated board where borax is applied for adjustment of starch viscosity.

In Recommendation XXXVI of the German Federal Institute for Risk assessment (BfR) [4], Borax usage is permitted, but not exceeding 0.005 % relating to the dry fibre pulp, as preserving agent for manufacturing of food contact papers. Additionally, application of sodium silicate, stabilized by 0.42 % Borax, as dewatering accelerator is permitted. Limits for the maximum level of borate in food contact papers do not exist either in Recommendation XXXVI of BfR or in the European Resolution AP (2002) 1 [5].

Figure 5 shows the amounts of borates determined in the cold water extracts of paper samples in 1991 and 2005 by spectrophotometry.

![Figure 5: Comparison of the amounts of borates in paper samples 1991 and 2005](image)

The determined concentrations of borates in the cold water extracts are comparable in both investigations (mean value 1991: 6.9 mg/kg paper; mean value 2005: 6.8 mg/kg paper). Furthermore, within the same paper grade no significant change of amounts of borates was identified. This is explained by the fact that the use of boron in chemical additives did not change over the investigated period. The accumulation of these inorganic ions on the surface of fibres does not occur. Due to their high solubility high shares of these compounds are discharged by the process water going to the effluent treatment plant.
Chloride, Fluoride, Bromide, Sulphate, Nitrate, Phosphate

Anions as components of dissociated salts occur in many environmental areas. Too high amounts of nitrates and phosphates have negative effects on the environment. Increased sulphate concentrations in circuit waters and effluents might induce corrosion on metal equipment and harm concrete. High amounts of chlorides in combustibles lead to increased hydrogen chloride emissions and contribute to the synthesis of dioxins and furans in high temperature processes with oxygen deficit.

Some inorganic additives used in the paper industry contain these anions, like aluminium sulphate as additive for resin sizing, dewatering and retention agents, for pH adjustment and precipitation agents in the mechanic chemical waste water treatment. Furthermore aluminium chloride, sulphuric acid (for pH-adjustment, bleaching processes and manufacturing of parchment paper), phosphoric acid (as nutrient in wastewater treatment plants) are also used. There is no limit for the maximum allowable concentration of these anions in food contact papers mentioned in the Recommendation XXXVI of the German BfR and in the European Resolution AP (2002) [1].

The current analyses of the inorganic anions are carried out by cold water extract of the paper samples and ionic chromatography. For bromide, fluoride, nitrate and phosphate the concentrations in the cold water extract were below the detection limit. These results are in line with the determined values from 1991.

The amounts of chloride in the cold water extract of the paper samples are very different between the different paper grades as shown in Figure 6. Some of the papers show lower chloride concentrations in the current samples, while others the concentration of chloride in 1991 was lower. Overall the mean value of the amounts of chloride in the 15 samples investigated was 238 mg/kg paper in 1991 compared to 232 mg/kg in 2005.

Figure 6: Comparison of amounts of chloride in the cold water extracts of paper samples in 1991 and in 2005

Figure 7 shows that the amounts of sulphate in the samples from 2005 are at a lower level than in the samples from 1991 (mean value 1991: 652 mg/kg, mean value 2005: 449 mg/kg). This is equivalent to a reduction of 31%. There is only one exception: a paper mill which produces grey board. In this paper mill aluminium sulphate is used as sizing agent and the mill has a closed water cycle and thus the paper samples had a sulphate amount of 5,597 mg/kg (1991: 4,350 mg/kg).
The decreased amount of sulphate could be explained by increase use of synthetic sizing agents where no aluminium sulphate is required for fixing the sizing agent to the fibre.

For the heavy metals only Nickel was investigated in the paper samples in 1991 and in 2005. In the current samples all determined amounts of Nickel were far below the detection limit as seen in 1991.

In summary it was observed that there is no accumulation of inorganic anions in the fibre circuit. Due to the water solubility and the low affinity to the fibres the inorganic anions are discharged by the process water going to the effluent treatment plant and thus removed from the fibre cycle. The determined amounts of these anions are therefore not the result of the accumulation of these substances in the paper, but a result of the added chemicals in the latest paper production process.

**Organic constituents**

**Halogenated organic compounds**

Most of the manufactured papers contain halogenated organic substances. Investigations regarding the origin and fate of these substances in the paper manufacturing process have shown that the most important sources of halogenated organic compounds in unprinted papers are chlorine bleached pulp, wet strength agents based on epichlorohydrin and chlorine treated industrial water [6, 7]. An additional source of halogenated organic substances in colour printed papers is yellow pigments (diaryl pigments) as constituents of printing inks.

Because of technical developments in the last years, especially the complete replacement of chlorine bleaching in Europe by TCF and ECF bleaching processes, a decrease in the amounts of halogenated organic compounds in paper is expected. Furthermore, the use of epichlorohydrin resins for the paper production is limited by regulations in food contact papers such as the Recommendation XXXVI of BfR.

To determine the amount of halogenated organic compounds in paper and board two different methods exist. The first one is the determination of Chlorine$_{organic}$ according to ISO 11480 and the second is the releasing of halogenated compounds in a cold water extract with a subsequent adsorption of these substances with activated carbon (AOX releasing).

The measured values for the amount of Chlorine$_{organic}$ confirm the assumption of their decreased concentration. In 2005 all paper samples investigated contain smaller amounts of halogenated substances in comparison to 1991 (see Figure 8). The amounts of chlorine-organic substances are considerable lower, especially in the samples which showed the highest amounts in 1991. As can be seen, the current paper sample No. 24 has an amount of halogenated
organic substances of only 9 % of the former concentration in 1991 and the samples 7 and 25 show an amount of 25 % of the former amounts.

Figure 8: Reduction of the amounts of halogenated organic compounds between 1991 and 2005

The mean value of all 15 paper samples is 103 mg/kg in 2005 in comparison to 260 mg/kg in 1991. The most effective process to reduce the amounts of halogenated organic compounds from the recovered paper is the deinking process during manufacturing of graphic papers and tissue papers.

The slightly higher amounts in tissue papers are the result of applying epichlorhydrin resins as wet strength agents. Packaging papers present the highest amounts of halogenated organic compounds because of the recovered paper processing without a deinking step.

The water soluble amount of halogenated organic compounds (AOX) confirms these results. The mean values are decreased from 3.1 mg/kg paper to 0.9 mg/kg paper.

Pentachlorophenol (PCP)

Pentachlorophenol was widely used in the past because of its fungicide and bactericide properties especially as wood preservative and leather preservative agent, as disinfectant and preserving agent. It is also used in great quantities as an algicide and fungicide. Because of its environmental and toxic effects the production volume and the use of PCP are now restricted. Since 1986 no PCP was produced in Germany. In 1989 the German Government passed a law to ban the use of PCP and its salts. The most important source for PCP in recycling paper today is the recovered paper, which origin is partly from abroad. Papers made from virgin fibres usually have PCP concentrations below the detection limit. The measured PCP amounts of the 15 investigated paper samples are shown in figure 9.
Regarding the acceptable amount of PCP in paper products, limits exist in the field of food contact papers (Recommendation XXXVI and ResAP (2002) 1) as well as in the scope of the environmental label „Blue Angel“ (RAL-UZ 5 „Sanitary Paper Products made of Recycled Paper“, RAL-UZ 14 „Recycled paper“, RAL-UZ 56 „Recycled Board“, RAL-UZ 72 „Printing and Publication Papers“). In all these regulations a maximum value of 150 µg/kg paper is fixed. In all current paper samples the measured PCP contents are far below this limit value.

Non-halogenated organic compounds

Diisopropynaphthalene (DIPN)

DIPN is used in the paper industry as solvent for color creating substances in the capsules of carbonless copy paper since the 1980’s. Before the use of DIPN, the very toxic PCB and later on chlorinated paraffin were used for this purpose. Because of fibre recycling traces of DIPN might occur in papers made from recycled fibres. By direct and/or indirect contact DIPN might migrate via gas phase into the food. In the last 10 years numerous investigations have been carried out regarding the amount of DIPN in food contact paper and in different foodstuffs [8, 9]. As shown in figure 10 the mean values of the DIPN concentrations in the recycling paper samples are not significantly different from 1991 (MV 29.5 mg/kg) to 2005 (MV 31.9 mg/kg).
In Germany no definite limit exists for the maximum allowed quantity of DIPN in food contact paper. In the Recommendation XXXVI of BfR and in the European Resolution is stated that the amount of DIPN in paper should be as low as possible.

Polycyclic aromatic hydrocarbons (PAH)

The most important sources of polycyclic aromatic hydrocarbons (PAH) in the recovered paper-new paper-circuit are the constituents of mineral oils in printing inks and carbon black pigments. Results of recent research work demonstrate that paper products with high ink coverage show significantly higher amounts of PAH than unprinted papers [10, [11]. A majority of PAHs are very carcinogenic thus their occurrence in paper products should be avoided. In food contact papers made from recovered paper, the limit given in Technical document No. 3 [12] has to be considered. No PAH might be detectable in foodstuffs (< 0.01 mg/kg foodstuffs). This regulation is essential for wet and fatty foodstuffs. PAH arise from imperfect combustion (oxygen deficiency) of organic matter. Formation of PAH during the paper manufacturing process is nearly impossible.

For the determination of PAH in paper samples a standardized test method does not exist. The analyses were carried out by gas chromatography coupled with mass spectrometry after extraction with n-hexane. 23 single substances from the class of PAH have been investigated. The limit of detection for each compounds is 0.02 and in some cases 0.03 mg/kg dry paper. The total PAH amounts (given as sum of the 23 substances) as well as the concentration values for the single substances are of interest for the evaluation of the results. In Figure 11 the total amounts of PAH are illustrated. The mean value in the paper samples from 1991 was 0.603 mg/kg, in 2005 only 0.424 mg/kg. The concentration of PAH has decreased in all the current paper samples compared to the samples from 1991 as one can see in Figure 11.
Figure 11: Amounts of PAH (Sum of 23 single substances)

The compound with the highest amounts in the current paper samples is phenanthrene with maximum amounts in some packaging papers up to 0.18 mg/kg. Benzo(a)pyrene and other compounds with high carcinogenic potential were not detectable.

Phthalates

Phthalates, the esters of phthalic acid, are as plasticizers very important industrial chemicals. They are added to PVC for coating materials, floorings, sealants, packaging materials, cables etc. They act as outer plasticizers, because the phthalates do not chemically bound to the polymer. Phthalates might thus be readily released by elution, migration and evaporation. Some of these compounds are reproduction toxic and mutagenic. Chemical analyses in the last years regarding the amount of different phthalates in papers have shown measurable amounts (> 5mg/kg) of Di-(2-ethylhexyl)phthalate and Di-n-butylphthalate. In paper manufacturing, phthalates are not purposely added, but might be present as parts of recipes for adhesive agents and plasticizers in additives for paper converting (for example in printing inks and glues).

To compare the amounts of particular phthalates the compounds with the highest production volume [Di-(2-ethylhexyl)phthalate (DEHP), Di-n-butylphthalate (DBP) and Di-iso-butylphthalate (DIBP)] are of special interest. In all papers originated from paper mills with a single or multistage deinking plant (all 3 graphic papers and all 3 tissue papers) neither DEHP nor DBP were detectable. In the 9 analysed packaging papers there is no consistent trend regarding the DEHP content. Nevertheless the amount of DBP is clearly reduced in all papers; the mean value decreased from 39.9 mg/kg in 1991 to 8.5 mg/kg in 2005. On the other hand the amounts of DIBP have increased. All 15 paper samples investigated in 2005 contained DIBP in measurable quantities (> 5 mg/kg). In 1991, however, in 6 paper samples the amounts of DIBP were not detectable. Even the papers manufactured today in paper mills with deinking plants show DIBP concentrations up to 20 mg/kg. The mean value of all 15 paper samples increased from 26.3 mg/kg to 64.5 mg/kg. The highest amounts of DIBP were observed in two different greyboards (150 and 170 mg/kg). The current investigations in Germany have found some dispersion adhesives as an important source of DIBP in recovered papers. Some representative and toxic substances of the phthalates are under restrictions and limits for sensitive applications (e.g. toys) are valid. DIBP is not listed in these regulations.

Other substances

Additionally other parameters have been investigated. The amount of disposable formaldehyde in the paper sample has significantly decreased in the last years. The increased use of formaldehyde-free wet strength agents and the

![Figure 11: Amounts of PAH (Sum of 23 single substances)](image-url)
optimization of formulations for manufacturing of formaldehyde resins regarding the complete cross linking of formaldehyde contributed to this reduction. Taking into account the grammage of the papers the determined formaldehyde amounts are at some orders of magnitude lower than the limits for food safety and the environmental label “Blue Angel”. The amount of primary aromatic amines has decreased as well. Regarding the releasing of antimicrobial substances, dye-stuffs and optical brighteners there were no significant difference between the samples from 1991 and 2005.

SUMMARY

The target of the current investigations was to determine if there is an accumulation of critical substances in papers due to the high recovered paper utilization rate and the higher number of recycling circuits. On the basis of the analytical investigations of 15 different recycled papers it was demonstrated that the amounts of problematical inorganic and organic constituents did not increase in spite of the tightened use of recovered paper.

Particularly the deinking plants in the recovered paper processing (flotation as well as wash deinking) are very effective sinks for removal of critical organic constituents from the fibre circuit. Two of the investigated packaging papers are manufactured with closed process water circulation. These papers show higher amounts of chloride and sulphate in comparison to the other packaging papers. The concentrations of the determined organic compounds, however, are not higher than in the other papers of this paper grade.

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