- Environment Innovation Program -
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Final Report

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Optimierte Ozonbehandlung zur weitergehenden Abwasserreinigung bei der Herstellung von Magazinpapier

Optimized ozonation for advanced wastewater treatment from production of magazine paper

Report no. 20241

UPM Plattling

- MD Papier GmbH -

Duration: June 2012 – September 2014

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Kurzfassung

Die MD Papier GmbH, ein Unternehmen der finnischen UPM Gruppe, betreibt am Standort Plattling die größte Papierfabrik zur Herstellung hochwertiger Magazinpapiere in Deutschland.

Mit Beginn einer neuen Formatproduktion steigt der Anteil an höhergebleichten Papiersorten. Durch die erforderliche intensivere Bleiche bei der Faseraufbereitung erhöht sich der Restanteil an biologisch nicht abbaubaren (persistenten) organischen Verbindungen im Ablauf der vorhandenen biologischen Abwasserreinigungsanlagen (ARA).

Im Ablauf einer vorhandenen Abwassereinigungslinie wird seit Jahren bereits eine Druckentspannungsflotation (DAF) zur Abtrennung von persistentem CSB mittels Fällung / Flockung betrieben. Um medienübergreifenden Nachteile durch den anfallenden Fällungsschlamm zukünftig vermeiden zu können, wurde eine optimierte Prozesskombination der bestehenden Behandlungsanlagen mit einem neuen tertiären Reinigungsverfahren umgesetzt.

Kernelement ist die Anwendung der partiellen chemischen Oxidation mit Ozon und biochemischen Oxidation durch Biofiltration in einer optimierten Ozonanwendung, die eine Reinigungsleistung deutlich über die Anforderungen der auf europäischer Ebene geforderten **B**esten **V**erfügbaren **T**echnik (BVT) hinaus aufweist. Das Verfahren wird der Gruppe der **A**dvanced **O**xidation **P**rocesses (AOP) zugerechnet. Eine wesentliche Zielsetzung ist die weitere Reduzierung der spezifischen Ozonmenge zur Elimination von persistentem CSB bezogen auf den Gesamtprozess und dadurch die Verbesserung der Energieeffizienz insgesamt.

Die gesteckten Ziele bei der großtechnischen Umsetzung einer optimierten Ozonanwendung in einem weiterentwickelten Ozonreaktorkonzept in Kombination mit einer Biofiltration wurden insgesamt mehr als erreicht:

- Die Sicherstellung einer nahezu vollständigen Ozonausnutzung unter atmosphärischen Bedingungen bei vergleichsweise hohen Ozoneintragsraten wurde erfolgreich umgesetzt (die Ozonausnutzung liegt im Mittel bei 99,9 %).
- Die geplante Eliminationsleistung von 1.320 kg/d CSB wurde mit einer installierten Ozonkapazität von 55 kg/h (bei 10 Gew.-% Ozon) mit bis zu 1.525 kg/d CSB eliminiert deutlich überschritten.

- Der spezifische Energieverbrauch bezogen auf den eliminierten CSB liegt bei der MD Papier GmbH mit 11,4 kWh/kg $COD_{elim.}$ um 45 % unter den Referenzangaben (vgl. 20,8 kWh/kg $COD_{elim.}$).
- Obwohl die hydraulische Kapazität der AOP für rund 55 % der Gesamtmenge vorgesehen ist, wurden die Betriebstage der vorhandenen Fällungsanlage (DAF) bereits um mehr als 80 % reduziert (höhere Effizienz und einfachere Prozesskontrolle der AOP im Vergleich zu DAF).
- Die Fällungsschlammmenge wurde entsprechend um mehr als 80 % gemindert und die verwertungstechnischen Nachteile dadurch erheblich reduziert.
- Das wesentliche Ziel, auch in Zukunft den Vorfluter Isar in einem sensiblen FFH Gebiet deutlich über die gesetzliche Mindestanforderungen hinaus zu schützen, wird mit der Reduzierung der organischen Restfracht auf 2,7 kg CSB pro t Papier (brutto) nachhaltig fortgeschrieben.
- Die effiziente Minderung darüber hinaus von AOX, Komplexbildnern und zu den prioritären Stoffen zuzuordnenden Spurenstoffen wie BPA, PAH sowie der deutlichen Reduzierung der endokrinen Wirkung des Abwassers zeigt das Potential für eine nachhaltige Verbesserung der Abwasserqualität bei der Anwendung des AOP-Verfahrens.

Das Erreichen eines Betriebsbereichs mit minimiertem spezifischen Ozonverbrauchs von 0,4 bis 0,6 kg Ozon pro kg CSB eliminiert wurde (noch) nicht erreicht (der Mittelwert beträgt 0,8 kg Ozon pro kg CSB eliminiert).

Das Potential um dieses Ziel zu erreichen, liegt in der Optimierung der partiellen Oxidation bei gleichzeitiger Erhöhung der Konzentration biologisch abbaubarer organischer Verbindungen (Erhöhung des BSB/CSB-Verhältnises) und deren biologischen Abbaus im Biofilter anstelle der rein chemischen Oxidation.

Die weiteren Optimierungsschritte sind im Bereich der Ozonreaktoren (Untersuchung der Effizienz bei unterschiedlicher Ozonverteilung je Reaktor, Betrieb von nur einem Reaktor bei niederer bis mittlerer Frachtelimination) sowie durch die Umsetzung einer frachtabhängigen über die TOC-online-Messung automatisierten Regelung geplant.

Keywords
Advanced oxidation process (AOP), persistenter CSB, cross-media, Mikroschadstoffe, bisphenol A, EDTA, DTPA, endokrine Wirkung, Ozonung, Biofiltration

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Abstract

The MD Papier GmbH, a subsidiary of the Finnish UPM Group and operating in Plattling, Lower Bavaria, is the largest papermill for the production of high-quality magazine papers in Germany.

When producing bright white papers, the paper manufacturing process necessitates a more intensive bleaching in the fiber preparation sequence, whereby the residual proportion of non-biodegradable (persistent) organic compounds in the treated effluent after the existing biological wastewater treatment plants increases.

In order to remove the additional persistent organic load and simultaneously avoid negative cross-media effects such as increasing precipitation sludge from the existing precipitation stage (DAF) methods from continually increasing the precipitation sludge in the future and to exploit the required cross-media aspects of further optimized performance an advanced tertiary treatment concept has been implemented.

The essential element of this treatment is the chemical / biochemical oxidation (chemical oxidation with ozone; biochemical oxidation with biofiltration) in a newly optimized ozone application representing an efficiency standard far above the European level of **B**est **A**vailable **T**echniques (BAT). The process is attributed to the group of **a**dvanced **o**xidation **p**rocesses (AOP). The objective of this application is a further reduction of the specific ozone consumption required for the removal of persistent COD and overall improved energy efficiency.

Overall, the objectives set into the large-scale application of the AOP, by applying a further developed ozonation reactor concept in combination with biolfilters and an overall optimized operation was more than achieved:

- Ensuring an almost entire ozone utilization (99.9 % are achieved in average) under atmospheric conditions at high ozone rates has been successfully implemented
- The target COD load reduction of 1,320 kg/d was surpassed (design parameters: installed ozone capacity 55 kg/h; 10 wt.-% with liquid oxygen (LOX) as carrier gas). COD elimination was up to 1,525 kg/d of COD.

- The specific energy consumption of the optimized AOP related to the eliminated COD is lower by 45 % for the AOP at MD Papier GmbH (11.4 kWh/kg$COD_{elim.}$) compared to the reference data according to BREF (20.8 kWh/kg$COD_{elim.}$).
- Although the hydraulic capacity of the AOP is up to 55 % of the total flow the number of operation days of the existing DAF could be substantially decreased by more than 80 % (higher efficiency and much better process control using AOP compared to DAF).
- The tertiary inorganic sludge amount of the DAF is accordingly reduced by over 80 % and the environmental disadvantages are substantially avoided.
- The main objective to significantly protect receiving river Isar in the future in a sensitive FFH area beyond the statutory minimum requirements will evolve sustainably with the reduction of the final organic residue discharge below 3.0 kg/t COD with an environmentally friendly process.
- An efficient reduction of micro pollutants (beyond of AOX and chelating agents) such as BPA, PAH and significant reduction of the endocrine disruptors shows the potential for a sustained improvement in effluent quality for the application of AOP.

The target to achieve a stable range between 0.4 - 0.6 kg ozone per kg of COD could not yet be reached (average is 0.8 kg ozone per kg of COD eliminated).

To achieve the objective of this is to optimize the partial oxidation while increasing the concentration of biodegradable organic compounds (increase of BOD/COD-ratio) and biodegradation in the biofiltration instead of purely chemical oxidation.

The further optimization steps are in the range of the ozone reactors (examination of efficiency with differing distribution of ozone per reactor, operation of only one reactor at low to medium load elimination) and in the online-TOC largely automated load dependent control.

Keywords
Advanced oxidation process (AOP), persistent COD, cross-media, micro pollutants, bisphenol A, EDTA, DTPA, endocrine disruptors, ozonation, biofiltration

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List of Figures

List of Tables

List of Abbreviations / Glossar

A	Area
AOP	Advanced Oxidation Process
AOX	Adsorbable Organic Halogenic Compounds
BAT	Best Available Technique
B_d	daily load
B_h	hourly load
BMUB	Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety
BOD	Biological Oxygen Demand
BPA	Bisphenol A
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
DTPA	Diethylene Triamine Pentaacetic Acid
EDTA	Ethylene Diamine Tetraacetic Acid
FFH-area	Flora-Fauna-Habitat area
HRT	Hydraulic Retention Time
IBC	Intermediate Bulk Container
Lab	Laboratory
LOD	Limit of detection
LOX	Liquid Oxygen
LWC	Light Weight Coated (Paper)
MBBR	Moving Bed Biofilm Reactor
MLSS	Mixed Liquor Suspended Solids
N_{inorg}	inorganic Nitrogen
O_2	Oxygen
O_3	Ozone
PAH	Polycyclic Aromatic Hydrocarbons
PFT	Perflourinated Tensides
p_{spec}	specific energy consumption
P_{tot}	total Phosphor
PCS	Process control system
Q_d	daily volume flow rate
Q_h	hourly volume flow rate
R&D	Research and Development
SC	Super-Calandered (Paper)
SS	Suspended Solid
t	Time
TOC	Total Organic Carbon
TOC	Temperature
UBA	Federal Environment Agency
V	Volume
WWTP	wastewater treatment plant
Wt-%	percentage by weight

1 Zusammenfassung / Executive Summary

1.1 Zusammenfassung

Ausgangssituation

Die MD Papier GmbH, ein Unternehmen der finnischen UPM Gruppe, betreibt am Standort Plattling die größte Papierfabrik zur Herstellung hochwertiger Magazinpapiere in Deutschland. Auf insgesamt drei Papiermaschinen werden gestrichene LWC-Papiere (LWC; lightweight coated) und ungestrichene SC-Papiere (SC; super-calandered) z. B. für Zeitschriften, Zeitungsbeilagen, Werbeprospekte sowie Verkaufs- und Versandkataloge erzeugt.

In Verbindung mit dem Aufbau einer neuen Formatproduktion seit Anfang 2012 wird bei der MD Papier GmbH ein größerer Anteil an hochwertigen höhergebleichten Papiersorten mit höherer Weiße erzeugt, ohne dass sich die Produktionskapazität ändert. Durch die im Papiererzeugungsprozess erforderliche intensivere Bleiche in der Faseraufbereitung erhöht sich der Restanteil an biologisch nicht abbaubaren (persistenten) organischen Verbindungen im Ablauf der vorhandenen biologischen Abwasserreinigungsanlagen (ARA).

Obwohl nach deutscher Abwasserverordnung und den zugehörigen branchenspezifischen Mindestanforderungen für Produktionen mit hochgebleichten Papiersorten spezifische CSB-Frachten bis zu 5,0 kg pro Tonne Papier zulässig sind, werden bei der MD Papier GmbH in Plattling durch die Anwendung von weitergehenden Abwasserreinigungsmaßnahmen zur Einhaltung der Umweltqualitätsziele in einem sensiblen FFH Gebiet bereits heute Ablaufwerte unter 3,15 kg CSB pro Tonne Papier erreicht. Für den Parameter CSB ist darüber hinaus die Einhaltung eines Überwachungswertes von 310 mg/l festgelegt.

Das Unternehmen will diese Umweltleistungen durch Umsetzung eines weitergehenden Abwasserreinigungskonzeptes zum Schutz der Isar fortschreiben. Das Konzept besteht aus einer optimierten Prozesskombination der bestehenden Behandlungsanlagen mit einer Ozonierung und einem Biofilter.

Vorhandene Anlagen zur weitergehenden Abwasserbehandlung

Die Abwasserreinigung bei der MD Papier GmbH erfolgte für die Abwässer aus LWC Produktion und SC Produktion aus historischen Gründen in zwei getrennten ARA's.

Bei der Erzeugung hochgebleichter Papiersorten erfolgte die weitergehende CSB Reduktion bei Bedarf ausschließlich im Ablauf der ARA aus der SC Linie durch Fällung mit dreiwerten Metallsalzen wie Aluminiumsalze oder Eisen(III) –salze und Abtrennung der geflockten Feststoffe durch Druckentspannungsflotation (DAF).

Die Anionen der Metallsalze (meist Chloride (Cl^-) oder Sulfate (SO_4^{2-}) bleiben gelöst und führen zu einer deutlichen Erhöhung des Elektrolytgehaltes im Abwasser. In der DAF werden mineralölhaltige Flockungshilfsmittel sowie Energie zur Drucklufterzeugung benötigt.

Der abgetrennte Fällungsschlamm ist schwer zu entwässern und mit einem hohen anorganischen Anteil nur bedingt zur Kompostierung geeignet.

Geplantes Verfahren

Die neue Anlage besteht aus einer optimierten Verfahrenskombination der bestehenden Behandlungsanlagen mit einem weiter entwickelten Ozonungs- und Biofiltrationsverfahren. Die Ozonstufe wurde als 2-stufiges unter Atmosphärendruck betriebenes Reaktorkonzept mit modularem Ozoneintrag in zwei getrennte Ozonreaktoren mit individuell regelbaren Ozoneintragssystemen ausgeführt.

Das Verfahren wird der Gruppe der **A**dvanced **O**xidation **P**rocesses (AOP) zugerechnet.

Ziele

Reduzierung Organik

Das Ziel dieser Prozessführung ist eine bestmögliche Anreicherung biologisch abbaubarer Stoffe durch partielle Oxidation persistenter organischer Verbindungen mit einem möglichst minimierten Ozoneintrag und die Vermeidung der unmittelbaren weiteren Oxidation dieser Stoffe in der Ozonstufe (und als Folge eines erhöhten Ozonverbrauchs). Die biologische Eliminationsleistung der gebildeten biologisch abbaubaren Verbindungen während der biologischen Filtration wird so auf möglichst hohem Niveau gehalten (und der Ozonverbrauch reduziert). Die erforderliche CSB Reduzierung beträgt bis zu 1,3 t/d.

Reduzierung Schlamm

Durch den Ersatz eines rein physikalischen Trennverfahrens und durch Vermeidung einer deutlichen Erweiterung der DAF soll die Erhöhung des überwiegend anorganischen Fällungsschlamms vermieden und der heutige Schlammanfall durch deutlich verminderten Einsatz der DAF (beschränkt auf Spitzenbelastungen) um mindestens $^2/_3$ reduziert (und nachteilige medienübergreifende Effekte deutlich vermindert) werden.

Energetische Optimierung

Eine wesentliche Zielsetzung ist die weitere Reduzierung der spezifischen Ozonmenge von 1,0 auf 0,4 - 0,6 kg Ozon pro kg CSB-eliminiert zur Elimination von persistentem CSB bezogen auf den Gesamtprozess und dadurch die Verbesserung der Energieeffizienz insgesamt.

Projektumsetzung

Die notwendigen Erweiterungs- und Optimierungsmaßnahmen beinhalten einen vernetzten Betrieb der vorhandenen Abwasserreinigungsanlagen sowie zusätzliche leistungssteigernde Maßnahmen innerhalb der ARA zur Sicherstellung einer bestmöglichen Reinigungsleistung und CSB-Elimination vor der weitergehenden Reinigung in neuen Anlagen.

Die Bemessungsabwassermenge für die AOP beträgt 12.000 m^3/d. Die installierte Ozonkapazität beträgt 55 kg/h bei 10 Gew.-% Ozon in flüssigem Sauerstoff (LOX) als Trägergas.

Bei der großtechnischen Ausführung wurden die Anbindungen so geplant, dass sowohl der Ablauf Nachklärung der ARA aus der LWC-Linie als auch der Ablauf Nachklärung aus der SC-Linie bei Bedarf der AOP behandelt werden.

Um das möglichst automatisch in einem neuen Regelkonzept steuern zu können, wurden zwei neu TOC-online Messgeräte im Ablauf der Nachklärung (entspricht dem Zulauf AOP) installiert und eine vorhandene TOC-online Messung in den Gesamtablauf installiert. Um eine automatische frachtabhängige Ozonregelung aufbauen zu können, werden seit Inbetriebnahme sowohl für den Ablauf ARA der SC-Linie als auch der LWC-Linie die notwendigen TOC und CSB Daten erfasst. Der automatisierte Betrieb konnte aber noch nicht umgesetzt werden, da eine umfassendere Datenbasis dafür erforderlich ist.

Die Umsetzung der Förderprojektes “Optimierte Ozonbehandlung zur weitergehenden Abwasserreinigung bei der Herstellung von Magazinpapier” bei MD Papier GmbH, Plattling, dauerte 15 Monate. Die AOP wurde ca. 12 Monate nach Baubeginn in Betrieb genommen.

Die statistische und grafische Auswertung zur Beurteilung der Leistungsdaten und Projektziele erfolgte für den Zeitraum August 2013 bis Anfang Oktober 2014 nach Inbetriebnahme.

Innerhalb dieser Phase wurde von August bis Oktober 2014 ein zusätzliches Messprogramm mit dem Fokus auf die Eliminationsleistung von AOX und Komplexbildnern sowie für eine Reihe prioritärer Spurenstoffe (z.B. Bisphenol A) und der endokrinen Wirkung des Abwassers durchgeführt.

Ergebnisse aus dem Testzeitraum und aus Untersuchungen zu medienübergreifenden Aspekten

Ozonausnutzung, spezifischer Ozonverbrauch

Ozonausnutzung

Die Ozonausnutzung in der Ozonstufe liegt im Mittel bei 99,9 % und ist damit fast vollständig.

(siehe Figure 19)

Eliminierte CSB-Fracht

Die geplante Eliminationsleistung von 1.320 kg/d CSB wurde mit einer installierten Ozonkapazität von 55 kg/h (bei 10 Gew.-% Ozon) mit bis zu 1.525 kg/d CSB eliminiert deutlich überschritten. *(siehe Figure 26)*

Spezifischer Ozonverbrauch

Der spezifische Ozonverbrauch basierend auf 24 h-Mischproben beträgt im Mittel 0,76 kg Ozon pro kg CSB eliminiert. Einzelne Werte im Normalbetrieb sowie aus großtechnischen Einzelversuchen liegen teilweise unter 0,6 kg Ozon pro kg CSB eliminiert.

(siehe Figure 26, Table 20)

Medienübergreifende Untersuchungen

Spezifischer Energieverbrauch zur Ozonerzeugung

Der spezifische Energieverbrauch zur Ozonerzeugung (Ozongenerator) beträgt durchschnittlich 7,8 kWh pro kg Ozon bei MD Papier GmbH im Vergleich zu 10 - 14 kWh pro kg Ozon nach Referenzangaben gemäß BREF. Der spezifische Energieverbrauch der AOP bei MD Papier GmbH liegt im Mittel bei 11,7 kWh pro kg Ozon (keine Referenzdaten im BREF verfügbar). *(siehe Table 20, Table 21)*

Spezifischer Energieverbrauch zur CSB-Elimination

Der spezifische Energieverbrauch bezogen auf den eliminierten CSB liegt bei der MD Papier GmbH mit 11,4 kWh/kg $COD_{elim.}$ um 45 % unter den Referenzangaben (vgl. 20,8 kWh/kg $COD_{elim.}$). *(siehe Table 20, Table 21)*

Minderung der Fällungsschlammmenge DAF

Die Betriebstage der DAF konnten von ca. 207 Tagen im Jahr 2012 (vor Betrieb der AOP) auf ca. 33 Tage bezogen auf den 12-monatigen Vergleichszeitraum reduziert werden (Minderung um 174 Tage entsprechend 86 %).

Die Schlammmenge verringerte sich um ca. 15.300 m^3 von rund 18.900 m^3 in 2012 auf rund 3.600 m^3 im Vergleichszeitraum entsprechend rund 81 %. Bei einer angenommenen TS-Konzentration im Fällungschlamm von ca. 35 g/l (gemessen aus Einzelwerten) entspricht dies einer Minderung von rund 535 t TS pro Jahr. *(siehe Figure 46, Table 20)*

Biologischer Überschussschlamm AOP

(berechnete Werte)

Der biologische Überschussschlammanfall aus den Biofiltern der AOP kann bezogen auf die eliminierte CSB-Fracht auf rund 40 t TS pro Jahr abgeschätzt werden. Dies entspricht einem Anteil von ca. 6 % bezogen auf den Fällungsschlammanfall in 2012 (ca. 662 t TS pro Jahr).

(siehe Figure 46, Table 20)

Spezifische CSB-Fracht zum Vorfluter

Die spezifische CSB-Fracht berechnet nach deutschen Mindestanforderungen liegt im Vergleichszeitraum bei 2,7 kg CSB pro t Papier (BMK) und berechnet nach BREF bei 2,5 kg CSB pro t Papier brutto. Wie oben erwähnt war die DAF noch ca. 33 Tage in Betrieb (siehe oben). Der Jahresmittelwert 2012 vor Inbetriebnahme der AOP zum Vergleich wird vom Betreiber mit 2,7 kg CSB pro t Papier brutto angegeben. Die spezifische CSB-Fracht zum Vorfluter wird bezogen auf 2012 knapp unterschritten ohne die Nachteile der DAF.

(siehe Table 24, Table 20)

Kostenbetrachtungen AOP, Vergleich mit Referenzangaben und DAF

Spezifische Betriebskosten bezogen auf CSB eliminiert

Die mittleren spezifischen Betriebskosten der AOP für Energie und LOX bezogen auf den eliminierten CSB betragen 1,64 € pro kg $CSB_{eliminiert}$ auf Basis spezifischer Betriebsmitteleinzelkosten 2014 für die AOP bei der MD Papier GmbH. Gemäß BREF werden mit Verweis auf Literaturangaben der Referenzanlage 1,33 pro kg $CSB_{eliminiert}$ angegeben. Unter Verwendung der (deutlich älteren und geringeren) veröffentlichten Betriebsmitteleinzelkosten der Referenzanlage, errechnen sich spezifische Betriebskosten von 1,14 € pro kg CSB eliminiert für die AOP bei der MD Papier GmbH in Plattling.

(siehe Table 24, Table 20)

Spezifische Betriebskosten bezogen auf die Bruttoproduktion

Die mittleren spezifischen Betriebskosten der AOP für Energie und LOX bezogen auf die Bruttoproduktion betragen 0,75 € pro Tonne Papier, brutto auf Basis spezifischer Betriebsmitteleinzelkosten 2014 für die AOP bei der MD Papier GmbH. Unter Verwendung der veröffentlichten Betriebsmitteleinzelkosten der Referenzanlage (siehe Anmerkung oben), errechnen sich spezifische Betriebskosten von 0,52 € pro Tonne Papier, brutto gegenüber 0,53 € pro Tonne Papier, brutto gemäß den Angaben nach BREF.

Spezifische Betriebskosten AOP im Vergleich zu DAF

Die spezifischen Betriebskosten sind kalkulierte Werte und beziehen sich auf mittlere CSB-Elimination und mittlere Verbräuche. Die Angaben werden auf die Menge bezogen, weil die Dosierung der Fäll- und Flockungshilfsmittel im Wesentlichen mengenproportional erfolgt.

Die mittleren Betriebskosten der AOP für Energie und LOX führen zu spezifischen Betriebskosten von ca. 7,4 ct pro m^3 und bei der DAF für Energie, Chemikalien und Schlammverwertung zu ca. 8,4 ct pro m^3.

(siehe Table 27)

Die spezifischen Betriebskosten der ARA für Betriebsmittel und Energie (ohne Schlammbehandlung und –verwertung) betragen 13,7 ct/m^3. Somit resultieren spezifischen Gesamtbehandlungskosten von 21,1 ct/m^3 mit AOP Betrieb bei mittlerer CSB-Elimination.

Elimination von AOX, Komplexbildner, Spurenstoffe und endokrin wirksame Stoffe

Ein wichtiger Bestandteil des Förderprojekts war die Untersuchung der Eliminationsleistung der AOP von AOX, Komplexbildnern, Spurenstoffen und endokrin wirksamen Stoffen. Über die zu untersuchenden Einzelstoffe und deren Abbauverhalten wurde in Abstimmung mit dem UBA und im Kontext mit dem Förderprogramm ein gesondertes zusätzliches Messprogramm vereinbart.

(siehe Table 6)

Obwohl die genannten Stoffe mit Ausnahme von AOX keine Überwachungswerte nach deutscher Rechtsverordnung und gemäß den branchenspezifischen Mindestanforderungen nach Anhang 28 für die Papierindustrie darstellen und die einzelnen Stoffe nur bei der Verwendung

bestimmter Rohstoffe und der Erzeugung bestimmter Papiersorten in nachweisbarer Konzentration im Abwasser vorkommen, ist die Untersuchung über die Elimination und das Abbauverhalten auf nationaler und internationaler Ebene von aktuell großem Interesse.

Die endokrine Wirkung in Abwässern der Papier- und Zellstoffindustrie wurde in den letzten Jahren intensiv untersucht und in Papierfabriken teilweise festgestellt, in denen überwiegend Altpapier als Rohstoff eingesetzt und über den Kreislauf bei der Papiererzeugung in den Kreislauf zurückgelangen.

Die Ergebnisse für ausgewählte Spurenstoffe, AOX, Komplexbildner und endokrine Wirkung sind nachfolgend zusammengestellt:

Abbau der Komplexbildner DTPA und EDTA

Der Abbau von Komplexbildner in der AOP wurde bei normalem Betrieb (Ozonerzeugung im Bereich ca. 25 – 40 kg/h) mit LWC und SC Abwasser sowie in einem großtechnischen Batchtest in einem Ozonreaktor bei voller Ozonproduktion (entsprechend bis zu 55 kg/h Ozon) mit LWC-Abwasser getestet.

DTPA-Abbau im Normalbetrieb

Die mittlere DTPA-Elimination wurde mit einem Wirkungsgrad von ca. 71 % in der Ozonstufe, mit ca. 19 % in der Biofiltration und mit 78 % in der AOP gesamt ermittelt.

(siehe Table 8)

EDTA-Abbau im Normalbetrieb

Die mittlere EDTA-Elimination betrug in der Ozonstufe ca. 62 %, in den Biofiltern ca. 14 % und in der AOP gesamt ca. 67 %.

(siehe Table 8)

DTPA / EDTA-Abbau im großtechnischen Batchtest (Ozonreaktor)

Der DTPA Abbau wurde mit 85 %, der EDTA Abbau mit 70 % ermittelt. Bei halber Ozonmenge wurde ein DTPA Abbau von 65 % und ein EDTA Abbau von 50 % gefunden.

(siehe Figure 39)

AOX-Abbau

Der AOX-Abbau wurde bei normalem Betrieb (Ozonerzeugung im Bereich ca. 25 – 40 kg/h) mit LWC und SC Abwasser sowie in einem großtechnischen Batchtest in einem Ozonreaktor bei Ozonproduktion mit Nennleistung (entsprechend bis zu 50 kg/h Ozon) für LWC-Abwasser getestet.

AOX-Abbau im Normalbetrieb

Der mittlere AOX-Abbau betrug in der Ozonstufe ca. 79 %, in den Biofiltern ca. 31 % und in der AOP gesamt ca. 76 %.

*(siehe Table 9**)***

AOX im Normalbetrieb im Gesamtabwasser

Die mittlere AOX-Konzentration im Gesamtabwasser betrug 0,2 mg/l an Tagen ohne Ozonbetrieb (die Biofilter sind im Dauerbetrieb) und 0,13 mg/l bei Betrieb der Ozonanlage, was einer Elimination im Gesamtabwasser vor Einleitung in die Isar von ca. 35 % entspricht.

AOX-Abbau im großtechnischen Batchtest mit LWC und SC Abwasser Ablauf ARA (Nachklärung)

Bei niederer AOX-Konzentration wurde zur Aufstockung Tetrachlormethan als AOX verwendet.

Die AOX-elimination betrug bis zu ca. 80 % im Verlauf der Ozondosierung bis rund 100 mg/l (was einer Ozonleistung von ca. 50 kg/h entspricht. Die Analysenergebnisse unterlagen je nach Labor (erwartungsgemäß) starken Schwankungen.

(siehe Table 11)

Abbau von Bisphenol A (BPA) (Endokrin wirksamer Stoff)

Abbau von Bisphenol A (BPA) unter normalen Produktionsbedingungen

Die BPA-Konzentration im Zulauf der ARA wurde mit 0,11 µg/l oder geringer bestimmt. Im Ablauf der ARA war die BPA-Konzentration unter der Nachweisgrenze, was auf die biologische Abbaubarkeit zurückgeführt wird.

Abbau von BPA im großtechnischen Batchtest

Zum Nachweis der Abbauleistung in der Ozonstufe wurde BPA im Reaktor bis auf ca. 0,09 µg/l aufgestockt. Die Nachweisgrenze von 0,04 µg/l wurde nach einer Ozonzugabe von knapp 60 g/m^3 erreicht, was einer Ozonerzeugung von ca. 30 kg/h entspricht.

Abbau von Polycyklische Aromatische Kohlenwasserstoffe (PAK)

PAK wurden im Abwasser Ablauf ARA der SC- und LWC-Linie untersucht (Werte im Nanogrammbereich). Für einige der untersuchten PAK-Verbindungen wurde ein Abbau von über 70 % in der AOP gemessen. Der Anstieg einzelner Stoffe in der AOP kann derzeit nicht erklärt werden.

Minderung von endokriner Wirkung

Die endokrine Wirkung im Abwasser der LWC-Linie wurde im Ablauf der ARA und der AOP mit einer speziellen Analysenmethode untersucht.

Im Ablauf der ARA wurde ein deutlich östrogenes Potential festgestellt (Induktionsrate 3,5 in der unverdünnten Probe), welches aber im Ablauf der Ozonstufe der AOP stark reduziert wurde (Induktionsrate 1,4 in der unverdünnten Probe; knapp unter der bisher festgelegten Grenze von 1,5). Im Ablauf der Biofilter der AOP konnte keine weitere Minderung nachgewiesen werden.

(siehe Kapitel 4.2.3.6)

Abbau von Phthalaten im Normalbetrieb

Die meisten der untersuchten Phthalatderivate (untersucht wurde ausschließlich SC-Abwasser) waren im Ablauf der ARA unter der jeweiligen Nachweisgrenze. Für zwei Phthalatderivate wurde in der Ozonung der AOP ein leichter Anstieg beobachtet, der in den Biofiltern wieder ausgeglichen wurde, so dass insgesamt kein Abbau dieser Stoffe in der AOP festgestellt werden konnte.

Abbau von Perfluorierten Verbindungen (PFC) im Normalbetrieb

Alle 11 im SC- und LWC-Abwasser untersuchten PFCs waren unter der Nachweisgrenze der betreffenden Stoffe. Der Abbau von PFCs durch aufstocken der Stoffe wurde nicht untersucht. *(siehe Table 19)*

Entfärbung

Die Entfärbung des Abwassers mit Ozon ist effizient und wird in einer deutschen Spezialfabrik großtechnisch angewendet.

Ausblick und Empfehlungen

Die gesteckten Ziele bei der großtechnischen Umsetzung einer optimierten Ozonanwendung in einem weiterentwickelten Ozonreaktorkonzept in Kombination mit einer Biofiltration wurden insgesamt mehr als erreicht:

- Die Sicherstellung einer nahezu vollständigen Ozonausnutzung unter atmosphärischen Bedingungen bei vergleichsweise hohen Ozoneintragsraten wurde erfolgreich umgesetzt.
- Die Bewertung medienübergreifender Aspekte zeigen für den maßgeblichen spezifischen Vergleichswert des Energiebedarfs bezogen auf den eliminierten CSB einen um ca. 45 % günstigeren Wert zu der Referenzanlage und somit eine deutliche Verbesserung der Energieeffizienz des angewendeten Verfahrens.
- Obwohl die hydraulische Kapazität der AOP für rund 55 % der Gesamtmenge vorgesehen ist, wurden die Betriebstage der vorhandenen Fällungsanlage (DAF) bereits um mehr als 80 % reduziert.
- Die Fällungsschlammmenge wurde entsprechend um mehr als 80 % gemindert und die verwertungstechnischen Nachteile dadurch erheblich reduziert.
- Das wesentliche Ziel, auch in Zukunft den Vorfluter Isar in einem sensiblen FFH Gebiet deutlich über die gesetzliche Mindestanforderungen hinaus zu schützen, wird mit der Reduzierung der organischen Restfracht auf 2,7 kg CSB pro t Papier (brutto) nachhaltig fortgeschrieben.
- Die effiziente Minderung darüber hinaus von AOX, Komplexbildnern und zu den prioritären Stoffen zuzuordnenden Spurenstoffen wie BPA, PAH sowie der deutlich Reduzierung der endokrinen Wirkung des Abwassers zeigt das Potential für eine nachhaltige Verbesserung der Abwasserqualität bei der Anwendung des AOP-Verfahrens.

Das Erreichen eines Betriebsbereichs mit minimiertem spezifischen Ozonverbrauchs von 0,4 bis 0,6 kg Ozon pro kg CSB eliminiert wurde (noch) nicht erreicht (der Mittelwert beträgt 0,8 kg Ozon / kg CSB eliminiert).

Das Potential um dieses Ziel zu erreichen, liegt in der Optimierung der partiellen Oxidation bei gleichzeitiger Erhöhung der Konzentration biologisch abbaubarer organischer Verbindungen (Erhöhung des BSB/CSB-Verhältnis) und deren biologischen Abbaus im Biofilter anstelle der rein chemischen Oxidation.

Um dies zu erreichen, sind folgende nächste Schritte geplant:

- Untersuchung der Effizienz bei unterschiedlicher Ozonverteilung je Reaktor (bisher erfolgt die Aufteilung gleichmäßig).
- Betrieb von nur einem Reaktor bei niederer bis mittlerer Frachtelimination.
- Untersuchung des Einflusses der hydraulischen Verweilzeit (Reduzierung der Abwassermenge bei gleicher Frachtelimination).
- Umsetzung einer frachtabhängigen über die TOC-online-Messungen automatisierten Regelung zur Kontrolle des optimalen Arbeitsbereichs und Reduzierung von Betriebskosten.

Die Betriebserfahrungen seit Inbetriebnahme zeigen, dass die Wahl eines möglichst flexiblen Systems vorteilhaft und notwendig ist, damit im praktischen Betrieb die Anpassungen für eine effektive Elimination gelöster Stoffe in Abhängigkeit der letztlich komplexen Reaktionskinetik zu ermöglichen.

Obwohl die diversen zusätzlich untersuchten Spurenstoffe und die endokrine Wirkung bereits meist unter der Nachweisgrenze im Ablauf der ARA bei der MD Papier GmbH gefunden wurden, zeigen insbesondere die großtechnischen Batchversuche, dass mit dem Betrieb der

AOP durch die überwiegend hohe Elimination dieser Stoffe bereits heute ein Beitrag zur Verbesserung der Wassergüte im Vorfluter Isar geleistet wird.

Die Umsetzung eines nachhaltigen Wassermanagements am Standort der MD Papier GmbH in Plattling ist Bestanteil der gesteckten hohen Umweltschutzziele der UPM-Gruppe.

Förderprogramme wie das BMUB-Innovationsprogramm ermöglichen die großtechnische Umsetzung innovativer Projekte. Die Betriebsergebnisse aus großtechnischen Anlagen und aus der fortlaufenden Optimierung im Dialog mit den regionalen und nationalen Fachbehörden liefern wertvolle Informationen, die auch für kommunales Abwasser und für Abwasser anderer Industriebranchen zur Fortschreibung des Standes der Technik genutzt werden können und so zur weiteren Verbesserung von Umweltleistungen beitragen.

1.2 Executive summary

Initial situation

The MD Papier GmbH, a subsidiary of the Finnish UPM Group and located at Plattling, is the largest papermill for the production of high-quality magazine papers in Germany. For example coated LWC paper (LWC: light-weight coated) and uncoated SC paper (SC: super calendared) for producing magazine paper, newspaper inserts, leaflets and sales and mail-order catalogues are generated on three paper machines.

At the beginning of 2012, a cut size paper production for high quality papers was implemented, whereby the amount of paper with a higher whiteness was further increased without affecting the total production capacity. When producing bright white papers, the paper manufacturing process necessitates a more intensive bleaching in the fiber preparation sequence, whereby the residual proportion of non-biodegradable (persistent) organic compounds in the treated effluent after the existing biological wastewater treatment plants increases.

Although, according to the German Wastewater Ordinance and the associated industry specific minimum requirements for manufacturing highly bleached paper and specific COD loads of up to 5.0 kg per tonne of paper are permitted, the MD Papier GmbH in Plattling, by applying tertiary wastewater treatment measures for COD reduction in the sensitive FFH environmental areas, lower specific COD loads of less than 3.15 kg COD per tonne of paper, have been achieved. In order to protect the river Isar, the local water authority demands a concentration monitoring value for the parameter COD of 310 mg/l, beyond the specific load requirement before discharge.

The company has decided to continue performing treatment by implementing an advanced wastewater treatment to protect the river Isar. The concept consists of an optimized treatment concept combining the existing treatment plants with ozonation and biofiltration.

Existing plants for tertiary wastewater treatment

For historical reasons the wastewater treatment at the MD Papier GmbH is performed in two separate wastewater treatment plants (WWTPs) - one for the LWC and one for SC production line.

When generating the highly bleached paper grades, the required tertiary COD reduction is performed in the final effluent of the SC line comprising precipitation with trivalent metal salts e.g. alum or iron salts and separation of the flocculated suspended solids with dissolved air flotation (DAF). The flotation also requires organic mineral oil-based polymers as a flocculant and energy for compressed air generation for DAF.

The dissolved anions of the metal salts (mostly chloride (Cl^-) or sulphates (SO_4^{2-})) remain dissolved and lead to a significant increase in the electrolyte content in the wastewater.

The separated precipitation sludge is difficult to dewater and, due to the high inorganic portion only restrictedly suitable for composting.

Planned process

The new facility consists of an optimized treatment concept combining the existing treatment plants with an advanced ozonation and biofiltration process. The ozone stage was designed as a two-stage reactor concept operated under atmospheric pressure with an individually controlled modular ozone entry system in the two separate ozone reactors.

The process is attributed to the group of **A**dvanced **O**xidation **P**rocesses (AOP).

Objectives

Reduction of organic compounds

The objective is the accumulation of biodegradable compounds by partial oxidation of persistent organic compounds with a minimized quantity of ozone and the avoidance of a further chemical oxidation of these substances (and an increased consumption of ozone). The biological elimination capacity of the formed biodegradable organic compounds during biological filtration stage is maintained at the highest possible level (and the ozone consumption is reduced). The required reduction in COD is up to 1.32 t/d.

Reduction of sludge

By replacing a purely physical separation process and by avoiding a significant enhancement of dissolved air flotation (DAF), an increase of predominantly inorganic tertiary sludge can be avoided. The objective is to reduce the precipitation sludge by considerably reducing the use of the DAF (limited to peak loads) by at least $^2/_3$ (and adverse cross-media effects are significantly reduced).

Energy optimization

A key objective is to further reduce the specific ozone consumption from 1.0 to 0.4 - 0.6 kg of ozone per kg COD eliminated for elimination of persistent COD based on the overall process, thereby improving overall energy efficiency.

Project implementation

The necessary expansion and optimization include a cross-linked operation of the existing facilities within the existing WWTP, as well as additional performance-enhancing measures within the ARA to improve performance with the goal to optimize the biological treatment performance and COD elimination in the WWTP prior to further wastewater treatment in new facilities.

The design flow of the AOP is 12,000 m^3/d. The installed ozone capacity amounts to 55 kg/h at 10 wt.-% in feed gas (LOX).

Advanced effluent treatment in the AOP is implemented either for the outlet secondary clarifier of the WWTP SC-line or for the outlet secondary clarifier LWC-line.

In order to automatically control the operation in a new operational concept, two new online TOC measurement devices in the course of the final clarifiers LWC- and SC-line (corresponds to the inlet AOP) were installed and an existing TOC online measurement installed in the total outflow (after merging the two effluent streams). Operation data for TOC and COD are continuously being collected since start-up to develop a strategy for a load-related ozone production control. However, the automated operation has not yet been implemented, since a more comprehensive database is needed for this.

The implementation of the project “optimized ozone application for advanced wastewater treatment for the production of magazine paper” at MD Papier GmbH, Plattling, lasted 15 months. The AOP went into operation 12 months after construction began.

The statistical and graphical analysis to assess the performance and project objectives after commissioning took place during the period August 2013 and early October 2014.

Within this phase, an additional measurement program with a focus on the elimination rate of AOX and non-readily degradable agents and for a number of micro pollutants (e.g. bisphenol A) as well as for endocrine disruptors was carried out.

Main results of the evaluation period and of cross-media effects of AOP

Ozone utilization, specific ozone consumption

Ozone utilization

The ozone utilization in the ozone stage is on average 99.9%, which is almost complete.

(see Figure 19)

COD-load eliminated

Up to 1,525 kg/d of COD are eliminated in the AOP with at installed ozone capacity of 55 kg/h. The planned elimination capacity of 1,320 kg/d COD is significantly exceeded.

(see Figure 26)

Specific ozone consumption

The specific ozone consumption is 0.8 kg ozone per kg of COD eliminated in average. Several data in normal operation and in a large-scale single test provide specific values below 0.6 kg ozone per kg of COD eliminated. *(see Figure 26, Table 20)*

Cross-media evaluations

Specific energy consumption for ozone generation

The specific energy consumption for the ozone generation amounts to an average of 7.8 kWh per kg of ozone at MD Papier GmbH in comparison to 10 – 14 kWh per kg of ozone as reference data according to BREF. The overall specific energy consumption of the AOP results in an average of 11.7 kWh per kg of ozone (no reference data available in the BREF). *(see Table 20, Table 21)*

Specific energy consumption

The specific energy consumption related to the eliminated COD is lower by 45 % for the AOP at MD Papier GmbH (11.4 kWh/kg$COD_{elim.}$) compared to the reference data (20.8 kWh/kg$COD_{elim.}$). *(see Table 20, Table 21)*

Reduction of tertiary sludge DAF

The operation days of the DAF could be reduced from 207 days in 2012 (prior to operation of the AOP) to approx. 33 days during a comparable 12 months within the evaluation period (Reduction is 174 days corresponding to 86 %).

The tertiary sludge volume is reduced by approx. 15,300 m^3 from approx. 18,900 m^3 in 2012 to approx. 3,600 m^3 within the evaluation period (corresponds to 81 %). This reduction amounts to approx. 535 t as dry substance with an estimated sludge concentration (measured from individual samples) of approx. 35 g/l. *(see Figure 46)*

Biological excess sludge AOP

(calculated values)

The biological excess sludge related to the eliminated COD amounts to approx. 40 t as dry matter per 12 months. This is equivalent to approx. 6 % related to the tertiary sludge quantity in 2012 before operation of the AOP (approx. 662 t TS p.a.). *(see Figure 46)*

Final COD discharge to receiving waters

Before the AOP went into operation in 2012, the annual average specific COD load to the receiving water amounted to 2.7 kg COD per tonne of paper gross. The achieved specific COD discharge related to the German minimum requirements after operation of the AOP amounts to 2.7 kg COD per t of paper produced and to 2.5 kg COD per t of paper gross

produced related to BREF which is the slightly lower but without the disadvantages of the DAF. As mentioned above, the DAF was only operated for approx. 33 days per year.

*(see Table 24, Table 20**)***

Economic analyses, comparison of reference data and DAF

Specific costs AOP related to COD eliminated

The specific operation costs related to the eliminated COD amount to 1.64 € per kg $COD_{elimi-nated}$ based on specific energy and LOX costs in 2014 compared to 1.33 € per kg $COD_{eliminated}$ according to BREF which are based on older (and much lower) costs for energy and LOX. The estimated specific costs taking the (much older and lower) cost bases according to published reference data (see also BREF) would amount to 1.14 € per kg COD eliminated at MD Papier GmbH. *(see Table 26, Table 20)*

Specific costs AOP related to gross production

The specific operation costs related to the gross paper production amount to approx. 0.75 € per t of paper gross when actual energy and LOX costs are considered. If the specific operation costs related to published reference data are considered (see remarks above) the specific operation costs related to the gross paper production are more or less within the same range (0.52 € per t of paper gross for the AOP at MD Papier GmbH, Plattling compared to 0.53 € per t of paper gross related to BREF). *(see Table 26)*

Economic analyses DAF and AOP

The specific operation costs are calculated values relating to the average COD elimination and average consumption data. The data are based on the flow rate because the dosing of chemicals is more or less flow proportional.

The calculated average operation costs for the AOP (energy, LOX) amounts to approx. 7.4 ct. per m^3 of effluent compared to 8.4 ct. per m^3 for the DAF (energy, chemicals, sludge utilization). Capital costs are not included. *(see Table 27)*

Elimination of micro pollutants and endocrine disruptors

An important part of the project was an additional measuring program for analyzing the elimination efficiency of micro pollutants and endocrine disruptors in the AOP although these parameters are not subject to the German Wastewater Ordinance and the associated industry-specific minimum requirements for the paper industry. However, the elimination efficiency of anthropogenic micro pollutants and endocrine disruptors is of major actual interest and is therefore included as agreed upon with the Federal Environmental Agency (UBA) in the context of the Environment Innovations' Program. *(see Table 6, Table 27)*

Endocrine disruptors were examined quite intensively in the pulp and paper industry and could be found in papermills when recovered paper is used as the main raw material (back pass over the circulation in the paper production).

The results for different selected micro pollutants, AOX and for endocrine disruptors are summarized below.

Chelating Agents DTPA and EDTA removal

The elimination tests for chelating agents were measured during normal AOP operation (ozone generation approx. 25 – 40 kg/h ozone) and in a large-scale batch test using one

ozone reactor only (up to full ozone capacity equivalent to 55 kg/h ozone generation) with LWC wastewater.

DTPA removal in normal operation

The average DTPA-elimination was determined with an efficiency of about 71% in the ozonation stage, with 19% in the biofiltration and in the AOP (ozonation plus biofiltration) with approx. 78%. *(see Table 8)*

EDTA removal in normal operation

The average elimination efficiency in the ozonation stage amounts to 62 %, in the biofiltration to 14 % and in the total AOP as much as 67 %. *(see Table 8)*

DTPA / EDTA removal in large scale batch test (one ozone reactor only)

The elimination of DTPA amounts to 85% and of EDTA to 70%. With only half of the ozone production, the elimination of DTPA amounts to 65% and for EDTA to 50%. *(see Figure 39)*

AOX removal

The elimination tests for AOX were measured during normal AOP operation (ozone generation approx. 25 – 40 kg/h ozone) and in a large-scale batch test using only one ozone reactor (up to full ozone capacity equivalent to 55 kg/h ozone generation) with LWC wastewater.

AOX removal AOP in normal operation

The average elimination efficiency in the ozonation stage amounts to approx. 79 %, in the biofiltration approx. 31 %, and in the total AOP as much as 76 %. *(see Table 9)*

AOX in the total effluent normal operation before discharge

The average AOX concentration in the total effluent amounts to 0.2 mg/l without operation of the AOP and to 0.13 mg/l with operation of the AOP. The continuous monitoring of AOX in the effluent to the river Isar (common effluent WWTP LWC and SC), required by wastewater permit, shows that the AOX could be decreased by an average of 35 %, when the AOP is in operation. *(see Table 10)*

AOX elimination in large-scale batch tests with effluent outlet WWTP

(Tetrachloromethane was added as an AOX source in cases where the AOX in the effluent was quite low)

The AOX elimination efficiency amounts to approx. 80 % when up to 98 g/m³ of ozone were injected (which is equivalent to an ozone generation of up to 50 kg/h). High variations in the AOX analyses, depending on laboratory, were observed (but this is often the case).

(see Table 11, Figure 40)

Bisphenol A (BPA) removal

BPA elimination in the WWTP under normal production conditions

BPA in the influent to the biological stage of the WWTP is very low (0.11 µg/l or lower). BPA at the outlet of the WWTP was below detection limit which was expected (due to the biodegradability and elimination in the WWTP). *(see Table 13)*

BPA removal in large-scale batch test (ozonation stage only)

The very low BPA content in the original wastewater was increased by adding of BPA up to 0.09 µg/l. The detection limit of 0.04 µg/l was reached after ozone diffusion of below 60 g/m^3 (which corresponds to approx. 30 kg/h ozone generation). *(see Table 14)*

Polycyclic Aromatic Hydrocarbons (PAHs) removal

A general elimination partly over 70% can be found. At the moment, there is no explanation for the increase of PAH in some cases. *(see Table 16)*

Endocrine disruptors removal

Endocrine disruptors can be found in recovered paper and wood. The measurement in the effluent was done during standard operation mode.

The significant estrogenic potential, which was determined in the effluent of the biological stage, (induction rate 3.5 in the undiluted sample) has been significantly reduced by the oxidative ozone treatment (induction rate 1.4 in the undiluted sample; just below the established limit of 1.5), not by biological degradation in the biofilter. *(see chapter 4.2.3.6)*

Phthalate removal in normal operation

Most of the investigated phthalate derivatives (SC wastewater was examined exclusively) were in the final effluent of the respective detection limit. For two phthalate derivatives, a slight increase was observed in the ozonation of AOP, which was compensated in the biofilters (no degradation of these substances could be detected in the AOP). *(see Table 17, Table 18)*

Perflourinated compounds (PFC) removal in normal operation

11 typical PFCs have been tested in the WWTP outlet of the LWC mill (which includes wastewater from deinking plant), but all values have been below detection limit and were not further examined. *(see Table 19)*

Coloring substances removal

The results of these tests demonstrate that treatment with ozone is a very efficient method for discoloration of papermill wastewater. This technique is already implemented in a specialty papermill. *(see Figure 42)*

Outlook and recommendations

Overall, the objectives set into the large-scale application of the optimized AOP, by applying a further developed innovative ozonation reactor concept in combination with biofilters was more than achieved:

- Ensuring an almost entire ozone utilization under atmospheric conditions at relatively high ozone rates has been successfully implemented.
- The cross-media evaluations for the specific electrical energy consumption per kg of COD eliminated provides an improvement of approx. 45 % and documents the enhanced energy efficiency of the optimized AOP concept.
- Although the hydraulic capacity of the AOP is up to 55 % of the total flow the number of operation days of the existing DAF could be substantially decreased by more than 80 %.

- The tertiary inorganic sludge amount is accordingly reduced by over 80 % and the environmental disadvantages for utilization are substantially avoided.
- The main objective in the future is to significantly protect the river Isar in a sensitive FFH conservation area beyond the minimum statutory requirements and sustainably develop the reduction of the final organic residue discharge below 2.7 kg/t COD with an environmentally friendly process.
- An efficient reduction beyond AOX, chelating agents and the priority substances associated micro pollutants such as BPA, PAH and of significantly reducing the endocrine disruptors shows the potential for a sustained improvement in effluent quality in the application of AOP.

The target to achieve a stable range between 0.4 - 0.6 kg ozone per kg of COD could not yet be reached (0.8 kg ozone per kg of COD eliminated is achieved on average).

To achieve this objective it is necessary to optimize the partial oxidation while simultaneously increasing the concentration of biodegradable organic compounds (increase of BOD/COD-ratio) and the biodegradation in the biofiltration instead of applying a pure chemical oxidation.

The optimization potential during operation, which could not yet be investigated, is the variable distribution of ozone per reactor (so far it is split evenly), the operation of only one reactor depending on the load to be eliminated, as well as the optimization of the hydraulic retention time (reducing or increasing the amount of wastewater within the possible operating range).

A general optimization potential is expected by applying a complete COD load depending ozone generation control using the TOC online signals inlet and outlet and a validated COD/TOC-ratio basis for an automated load depending process control to avoid a far reaching COD elimination below the required optimum.

With the implementation of a load dependent on the TOC-online measurements automated control, the optimum operating range can generally be monitored and the operating costs are further reduced.

The operational experiences gained since this rather short operation period already show that choosing a flexible process with adjustable operation conditions is beneficial and necessary to ensure that the practical operation will allow the required adjustments for effective elimination of solutes as a function of the ultimate complex reaction kinetics.

Although micro pollutants and endocrine disrupters are found near or below the detection limit after the WWTP at MD Papier GmbH the results of the batch test show that the high elimination efficiency for many of these substances by applying AOP will help to improve the water quality of the receiving waters even in the future.

The implementation of a sustainable water management is in accordance with the policy of high environmental protection objectives within the UPM Group in general and on site at MD Papier GmbH Plattling.

Funding programs such as the BMBU Environment Innovation Program of the Federal Environmental Ministry (BMUB) enable the large-scale implementation of such innovative projects.

The operating results of industrial plants and from the continuous improvement in dialogue with regional and national expert authorities provide valuable information that can be used for municipal wastewater and for wastewater from other industrial sectors updating the state of the art and thus contribute to further improvement of environmental performance.

2 Introduction

2.1 Short description of the company

The papermills operated by MD Papier GmbH and Rhein Papier GmbH belong to the Finnish company UPM Kymmene Oyj, one of the worldwide leaders in paper production. MD Papier GmbH, as the owner of the common wastewater treatment plant and therefore the holder of the water relevant permits, will be named in this report and represents both companies. The largest UPM papermill in Germany for the production of magazine paper is MD Papier GmbH located in Plattling.

2.2 Short description of the paper production

LWC (***L***ight-***W***eight ***C***oated) paper grades and uncoated SC (***S***uper-***C***alandered) paper grades for producing magazines paper, newspaper inserts, leaflets and sales and mail-order catalogues are generated on three paper machines. Production capacity per year amounts to approx. 790,000 t on the whole site.

When high brightness grades are manufactured, the paper manufacturing process necessitates a more intensive bleaching in the mechanical pulp preparation associated with higher demands of poorly biodegradable chemical additives, caustic soda (NaOH), peroxide (H_2O_2), chelating agents (DTPA, EDTA), whereby the residual proportion of non-biodegradable (persistent) organic compounds in the treated effluent after the existing biological wastewater treatment plants increases. Due to the amount of remaining persistent organic compounds the parameter COD (load and concentration) increases in the outflow of the secondary clarifiers since the specific water consumption remains unchanged.

Since May 2012 format paper production was additionally implemented at MD Papier GmbH in Plattling requiring highly bleached paper grades due to the high brightness. Extra intensive bleaching again increases non-biodegradable organic compounds in the wastewater.

However, it is therefore important, that the optimization potentials in the existing WWTPs are fully exploited to achieve a complete biological degradation in biological wastewater treatment stages and the lowest possible COD concentration before advanced effluent treatment.

2.3 Legal standards for wastewater discharge

According to German Wastewater Ordinance and the associated industry-specific minimum requirements for manufacturing highly bleached paper and specific COD loads of up to 5.0 kg per tonne of paper may be allowed [AbwV (2004)]. In order to protect the Isar river, the

local water authority demands an emission limit value of 310 mg/l COD, the national minimum requirement for discharge.

In order to meet this requirement, the MD Papier GmbH in Plattling has to apply tertiary wastewater treatment measures for COD reducing the specific loads to below 3.15 kg COD per tonne of paper.

To comply with the existing national and international environmental legal requirements in a sensitive FFH environmental area, the company has decided to implement a new wastewater treatment concept. Environmental protection in wastewater treatment at MD Papier GmbH in Plattling is therefore kept on a national and international leading level.

2.4 Initial situation and concept development

2.4.1 Initial situation

For historical reasons the wastewater treatment at the MD Papier GmbH is performed in two separate wastewater treatment plants (WWTPs) - one for the LWC and one for SC production line.

When generating highly bleached paper grades, the required tertiary COD reduction is performed in the final effluent of the SC line. A pure separation process comprising precipitation, flocculation and separation with dissolved air flotation (DAF) is used. The precipitation / flocculation persistent COD compounds require intensive doses of inorganic precipitants (typically trivalent metal salts based on aluminium (Al^{3+}) or iron (Fe^{3+})). The flotation also requires organic mineral oil-based polymers as a flocculant and energy for compressed air generation for DAF. While the trivalent metals (cations), mainly metal hydroxide ($Fe(OH)_3$ or $Al(OH)_3$), are precipitated with the organic substances (COD to be reduced), the electrolyte content of the remaining dissolved anions (usually chloride (Cl^-) or sulphate (SO_4^{2-})) increases significantly in the wastewater.

The primary sludge from the mechanical sedimentation and secondary biological excess sludge of the WWTP's is dewatered in separate sludge dewatering lines due to the different sludge utilisation (see chapter 2.4.2. existing sludge treatment).

The precipitation sludge from the DAF, which is difficult to dewater because of the bad sludge characteristics of the metal hydroxide sludge, (which tends to clog the sieve surfaces of the dewatering machines) must be mixed with the biological excess sludge and also with primary sludge. Only this procedure enables sufficient minimum dry matter content and a recycling by composting after the sludge dewatering. The inorganic portion of the precipitated sludge for composting is ecologically detrimental. The integration of the precipitation sludge in the

primary sludge line is not possible due to the unfavourable drainage properties of the precipitation sludge, as described above.

In order to avoid ecologically adverse effects from continually increasing amounts of precipitation sludge in the future, the new concept should reduce the amount of precipitation sludge by using alternative treatment techniques.

2.4.2 Description of the existing wastewater treatment plants

The **primary** (chemical / mechanical) **treatment** of the raw effluent from the SC and LWC production consists of the following main treatment stages

- Automatic coarse and fine screen for removing coarse solids
- Hydraulic buffer
- Neutralisation (LWC wastewater only)
- Primary clarifier for removal of suspended solids
- Indirect cooling with heat exchanger and cooling tower before two-stage aerobic biological treatment

S**econdary treatment** according to BAT:

- Moving bed biofilm reactor with carrier media (two-stage reactor)
- Low loaded activated sludge system
- Secondary clarification

A tertiary treatment consisting of chemical precipitation / flocculation and dissolved air flotation is installed for tertiary treatment of the SC wastewater outlet WWTP of the SC line. The main treatment stages WWTP SC and LWC are shown **in Figure 1**.

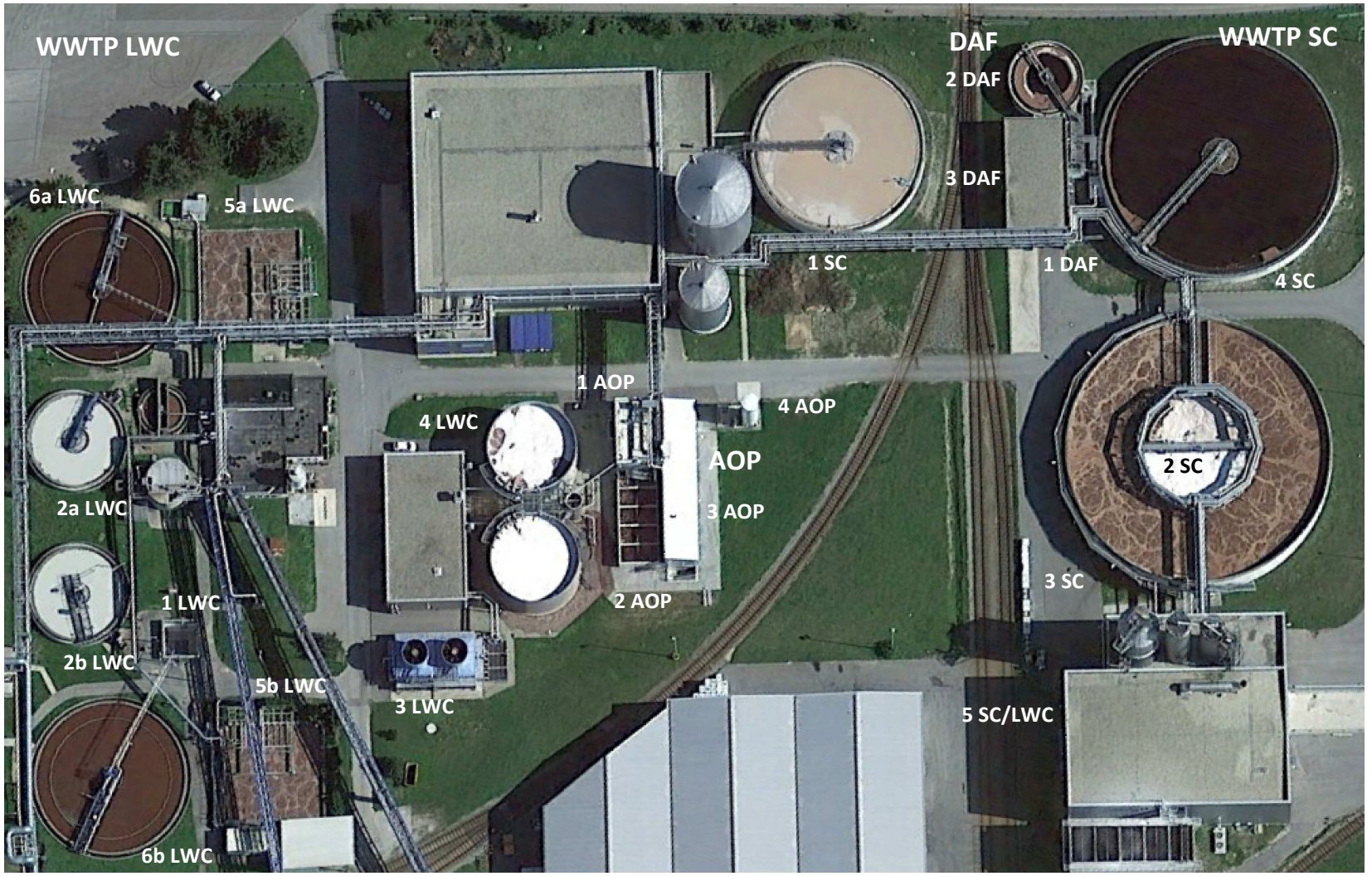

Figure 1: View WWTP LWC and WWTP SC with new AOP at MD Papier GmbH, Plattling (source: google earth, December 2014; the added numbers in Figure 1 are explained below)

Figure 1: The effluent of the WWTP LWC is neutralised (1 LWC), mechanically clarified in the primary clarifiers (2 a, b LWC) and cooled (3 LWC). The effluent of the WWTP SC is mechanically clarified in the primary clarifier (1 SC).

After primary treatment the effluent of the SC- and LWC lines are each treated in two-stage aerobic treatment stages according to BAT treatment technologies. Each line consists of a high loaded aerobic stage (moving bed biofilm reactor with carrier media) (4 LWC, 2 SC) followed by a low loaded activated sludge system and secondary clarification (5a,b LWC, 6a,b LWC and 3 SC, 4 SC). Only the SC-line is equipped with a classical tertiary treatment process for precipitation, flocculation (1 DAF with chemical preparation 3 DAF) of organic substances (COD to be removed) Dissolved air flotation (DAF) (2 DAF) is applied for separation of the produced suspended solids (production of tertiary sludge).

The primary, secondary and tertiary sludge is dewatered in sludge dewatering building (5 SC/LWC).

The biological treated effluent outlet of the secondary clarifiers (COD load and concentration) can be decreased by precipitation and flocculation by about 30 to 40 % using an excessive amount of trivalent metals. Organic substances are separated and not eliminated in this pure separation process that characterises a negative cross-media effect under environmental aspects as described above.

Existing sludge treatment

Preconditions for sludge utilisation

The papermill at MD Papier GmbH does not have its own incineration for thermal utilisation of the sludges. The dewatered primary sludges from the WWTP's are utilized in the cement and brick industry. The tertiary precipitation sludge from the DAF must be mixed with the biological excess sludge and with primary sludge to enable a sufficient minimum dry matter content and a utilisation by composting after the sludge dewatering. The sludge dewatering and utilisation of tertiary precipitation sludge alone is technically not reliable.

Primary sludge treatment

The suspended solids from the papermills are removed by physical sedimentation in primary clarifiers before biological treatment. The settled suspended solids are pre-thickened in an integrated thickening zone and are finally dewatered in a screw press.

Biological excess sludge and tertiary precipitation sludge treatment

The biological excess thin sludge from the secondary clarifiers either has to be pre-thickened in a static thickener tank in the LWC line or in an integrated thickening zone in the secondary clarifier in the SC line to enable the mechanical sludge dewatering with the existing belt filter press. An increased hydraulic retention time in the static thickeners can lead to higher sludge concentration of the pre-thickened excess sludge which is favourable for the dewatering especially in the case that tertiary precipitation sludge has be dewatered together with the excess sludge.

The tertiary sludge (typically < 10 wt.-%) has to be mixed as a minor part with biological excess sludge plus primary sludge (typically > 40 wt.-%). Only the sludge mixture can be dewatered up to a dryness of approx. 30 % dry solids with the existing sludge belt filter press. The dewatered mixed sludge (which leads by the required addition of primary sludge to an increased volume) including the parts of inorganic tertiary and primary sludge is further utilized for composting at comparatively high sludge disposal costs compared to the sludge disposal of the primary sludge alone.

The objective is to reduce precipitation sludge and the remaining part of primary sludge for dewatering and to reduce the inorganic part in general for further utilisation by composting.

Negative effects from static pre-thickeners for biological excess sludge

Sludge storage in the integrated pre-thickening zone of the secondary clarifier WWTP SC-line can influence the operation of the activated sludge system directly in a negative way especially when the activated sludge is stored for pre-thickening in the clarifier (risk of damage to the activated sludge biocenosis due to anoxic conditions as mentioned above and resolution of eliminated organics).

The disadvantage of static thickeners of the secondary clarifiers WWTP LWC-line is that due to the long HRT and under anoxic conditions, anaerobic decomposition might occur. The risk of odour development during sludge dewatering rises in addition. The filtrates of the sludge dewatering which are pumped back to inlet of the bio-stage can lead to increased oxygen consumption and can disturb the aerobic biodegradation process. An increase of the sludge volume index is observed under these conditions. Suspended solids at the outlet of the secondary clarifiers can be increased which has to be avoided. A suspended solids removal efficiency to achieve less than 15 mg/l SS in average is required when tertiary treatment is applied (consumption of ozone would increase in the AOP process if the SS exceeds above this level).

The objective is to by-pass the static thickeners after reduction of the precipitation sludge in an optimized sludge dewatering concept. (see detailed information chapter 3.5.1)

2.4.3 Advanced oxidation processes in theory

2.4.3.1 Ozone Application

Ozone is used in applications for industrial purposes and for water and wastewater treatment and is generated in a carrier gas. As a result, an ozonation reactor is at least a two-phase system, consisting of the gas phase carrying the ozone and the fluid or product phase (generally contained in a liquid) where the ozone must be transferred for chemical reaction [Helble, Schlayer, Liechti, Jenny, Möbius (1999)].

The absolute level of the ”partial pressure” of ozone is one of the main design parameters, essential to control the efficiency of both the task which ozone is assigned to perform and the kinetics of the chemical reactions.

Since one is dealing with at least a two-phase system (or a three phase system in the case of a high suspended solids load in a liquid), the way in which the two respectively the three phases are brought into intimate contact is essential. The ”mixing energy” and whether this energy has a ”macroscopic or turbulent” (macroeddies) or a ”microscopic or laminar” (microeddies) character as well as the ”hydrodynamic pattern” (fullmix, plug-flow, cocurrent, countercurrent) of the ozonation reactor are main design and control parameters for the task assigned to the ozone.

Secondary reactions of ozone with the by-products of the primary reactions are in most cases unwanted since they lead to increased ozone consumption and to higher costs. They must be controlled with the best possible efficiency. Unlike with oxidation chemicals, which are directly mixed as a liquid solute with the fluid to be treated, such secondary reactions can be controlled in an ozonation system more easily.

Ozone diffusion model

A ”gas-liquid” system requires the formation of a ”gas to liquid interface”. This feature and as a consequence the advantage of such a system is the fact that this ”interface” carries a ”liquid film”, which separates the ”bulk” of the liquid from the ”interface”. Depending upon the degree and pattern of turbulence this ”film” can be strongly attached to the interface or periodically replaced. It is possible to control where the reactions with ozone shall predominantly take place, either immediately under the ”interface” at the liquid side, or in the ”film” or in the ”bulk” of the liquid. In a same fashion, the hydrodynamics around the ”liquid film” can also be influenced.

The model for liquid film, bulk and interface reactions in a stable ”plug-flow ”co-current bubble column is shown in **Figure 2** - **Figure 4**: Ozone diffusion ”bulk”-reaction [Hoigné (1988)].

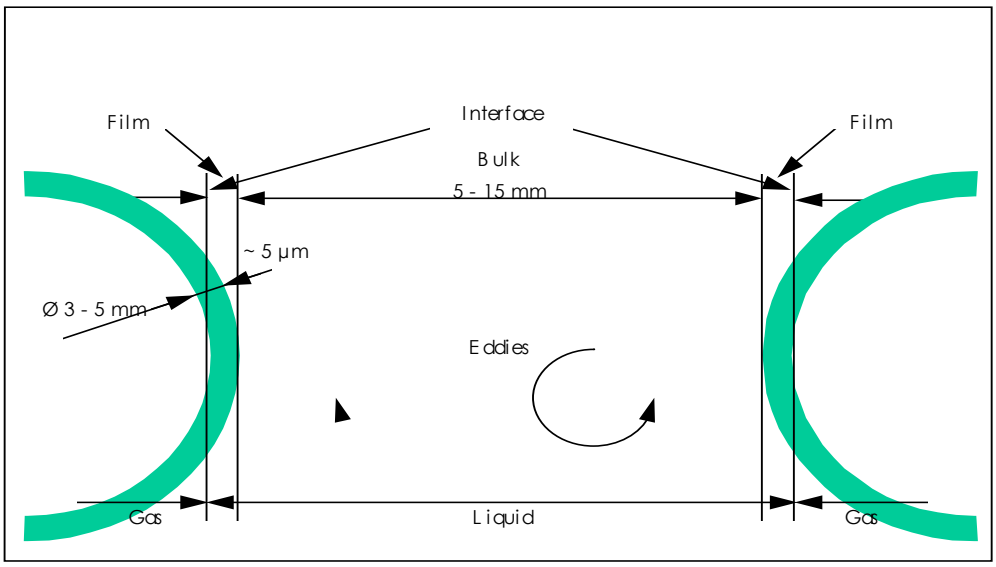

Figure 2: Ozone film model

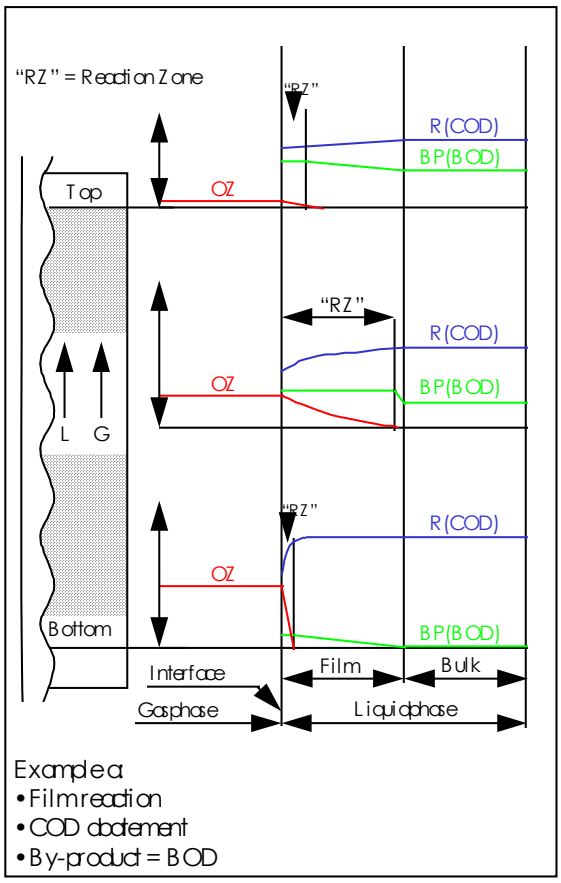

Figure 3: Ozone diffusion ”film”-reaction

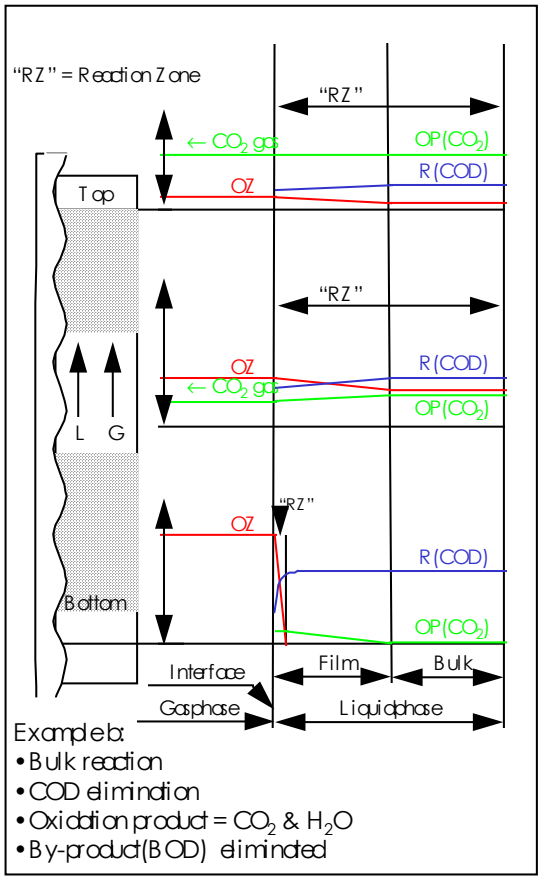

Figure 4: Ozone diffusion ”bulk”-reaction

Figure 3: Ozone diffusion ”film”-reaction shows schematically an idealized plug-flow co-current ozone reaction balance room in which the chemical reaction for partial oxidation of the persistent COD (Reactant R (COD)) with ozone shall take place predominantly controlled as a film zone. Built by-products (BP) (which are bio-degradable (BOD)) diffuse into to the bulk zone. The by-product (BOD) increases while the reactant (COD) in the bulk stays on the same level or is only slightly reduced. As a consequence the BOD/COD-ratio at the outlet of the balance room is increased. The wastewater can be treated for further COD removal by biochemical oxidation in a downstream bioreactor (biofiltration).

Efficient mixing, a large surface (which is provided by fine bubbles), a sufficient HRT and reaction conditions which depend on the ozone partial pressure (atmospheric pressure conditions) are the most important parameters to be controlled.

Figure 4: Ozone diffusion ”bulk”-reaction shows schematically an idealized plug-flow co-current ozone reaction balance room in which the chemical reaction on of the persistent COD (Reactant R (COD)) with ozone shall be predominantly controlled as a bulk zone. Due to the chemical reaction in the bulk built by-products (BP) are oxidized to CO_2 which partially is stripped out depending on the lime / carbonic acid equilibrium. As a consequence the reactant (COD) in the bulk is continuously reduced but by a steadily consumption of ozone in the bulk. As a consequence there is no (or much less) BOD/COD-ratio increase at the outlet of the balance room. No efficient biochemical oxidation in a downstream would be possible.

Efficient mixing and reaction conditions where ozone diffuses into the bulk (conditions under pressure) are important parameters to be controlled.

With the use of the three design parameters ”ozone partial pressure”, ”mixing energy” and ”hydrodynamic pattern” and an indispensable knowledge of the chemistry involved and its kinetics, the performance of an ozonation system can be optimized.

2.4.3.2 Biological Filtration

The effluent treatment with fixed bed biofilm reactors (biofilters) is an aerated upflow filtration process. The practical experiences show that the biological upflow filtration - depending on the type of problem – is particularly suitable to eliminate carbon, ammonium, nitrogen and phosphorus. At the same time, an advanced removal of the suspended solids takes place.

The system is shown schematically in **Figure 5**.

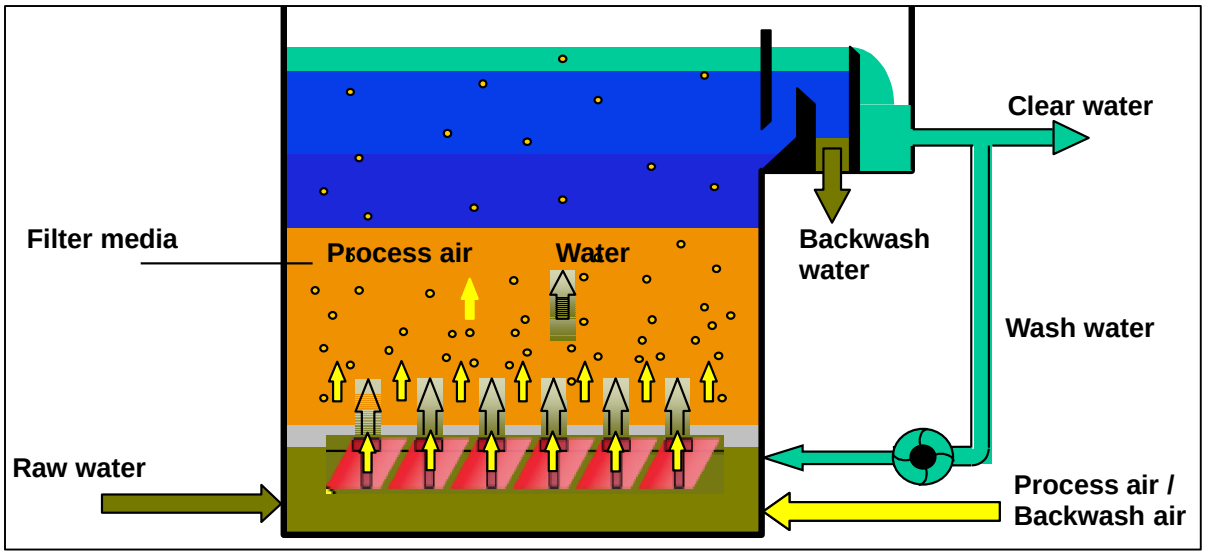

Figure 5: Schematic view biofiltration

The oxygen needed for the oxidation of carbon and ammonium is distributed by a process air diffuser below the strainer plate. Thus a regular oxygen supply over the total filter cross-section can be assured. In the case of denitrification (mainly for municipal wastewater treatment) a carbon source such as raw sewage or methanol is added via a separate diffuser above the strainer plate. Depending on the type of problem the height of the filter material can be varied between 2 - 4 m. By choosing the appropriate filter material a high concentration of attached bio-mass and a high suspended solids retention can be guaranteed simultaneously. To this end, filter materials with rough and porous surface (BIOLITE) are particularly suitable. The suitable combination of filter material and adapted backwashing (sequence of air/water and following water washing) guarantees optimal filter cleaning procedures. These measures ensure the stable and secure operation of such filters and the reduction of noise and odour emission.

The biofilters can be installed - as shown in Figure 5 - modularly and very compact so that space requirement can be reduced.

The biological filtration is three phases system with

- A solid phase, i.e. the filter material with attached bio-mass
- A liquid phase, i.e. the wastewater that passes through the filter material
- a gaseous phase, i.e. e. the oxygen to assure oxidative processes or the gaseous nitrogen when denitrification takes place.

Present experience shows that the principle of co-current of liquid and gaseous phases - as realised in the biological upflow filter - is superior to the other processes (such as the counter-current process in biological down flow filter) regarding process and operation.

2.4.3.3 Ozonation and biofiltration combined to AOP

The applied AOP process is the combined process of ozonation (chemical oxidation) followed by biological filtration (biochemical oxidation). AOP is applied to a completely biologically treated effluent.

Target of the process design in the chemical oxidation stage is the partial oxidation of the remaining persistent compounds and transformation into biodegradable compounds, which can be biologically eliminated in the biofiltration stage.

This combination is ecologically preferable and allows economic optimization. With reduced use of expensive chemical oxidants persistent COD becomes biodegradable. The partially oxidized compounds are eliminated in the downstream bioreactor.

Parts of these persistent compounds require a comparatively long chemical reaction time of several minutes for partial degradation. The hydraulic retention time in the ozone reactor and a most efficient distribution of ozone into the wastewater has to be considered in the reactor design.

This process has achieved a high reputation whenever the elimination achieved in a tertiary biofilter is not sufficient.

Due to the relatively low concentrations of biodegradable compounds following the partial oxidation for the subsequent bio-treatment, only biofilm reactors can be used. The tertiary biofilters used in this project are the only biofilm systems tested because so far they appear to be the best suitable type of reactor. The combination still has to be optimized technically and economically to achieve best possible results with minimum costs. The improvement of the energy efficiency is one of the main objectives for further optimizations of the process.

A schematic presentation of this process is given in **Figure 6**:

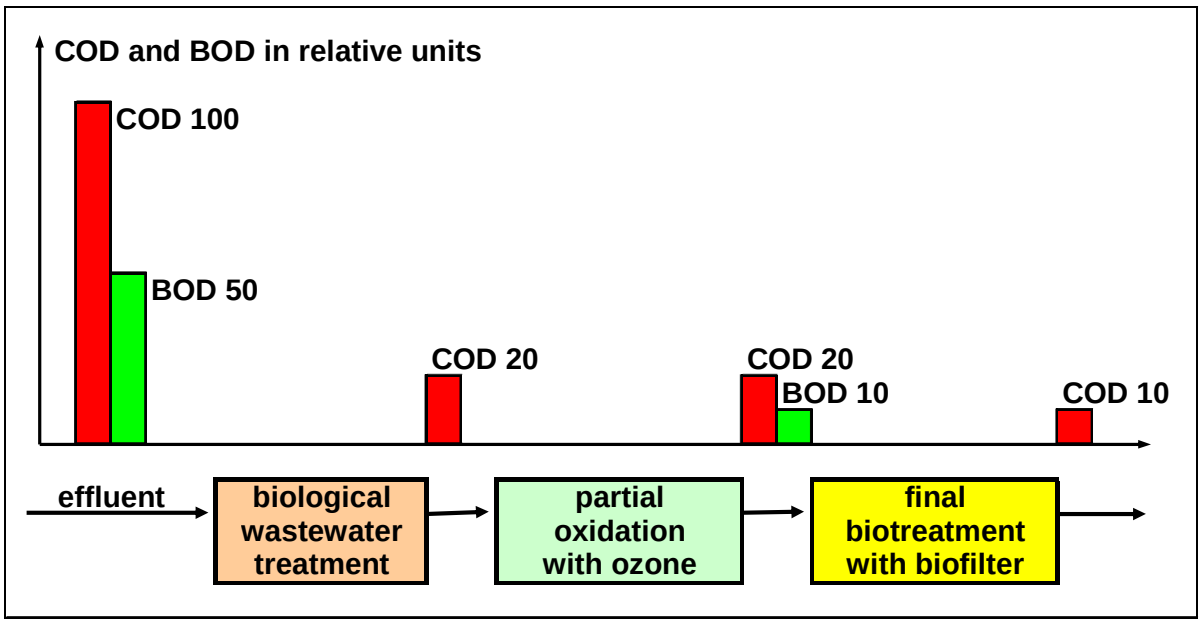

Figure 6: Schematic presentation of the process of chemical-biochemical oxidation of papermill wastewater

This combined process conducted in single-stage version has a COD removal efficiency up to 50 % and in two-stage version up to 80 %. [Möbius, Helble (2004)]. The biological excess sludge of the biofiltration stage can be dewatered in the sludge treatment together with the secondary excess sludge.

High elimination rates of persistent COD and other compounds are achieved simultaneously, such as:

- AOX
- color
- chelating agents (i. e. DTPA, EDTA)
- optical brighteners
- surface active substances
- micro pollutants
- microorganism (disinfection)

The tertiary treated effluent by AOP is predestined for effluent reuse and to decrease the fresh water consumption.

2.4.4 AOP at MD Papier GmbH, Plattling

The essential element of the optimization measures is generated by the extension of the WWTP applying an ecologically preferable new treatment concept using a chemical / biochemical oxidation process instead of physical separation.

The process can be classified within the group of **Advanced Oxidation Processes** and will be further defined as **AOP** [Möbius, Cordier, Helble, Kaulbach, Cordes-Tolle (1996], [Möbius (1999), (2006), (2010)].

The setup of the AOP as the essential technological element for an optimized advanced wastewater treatment is shown as a simplified flow sheet in **Figure 7**.

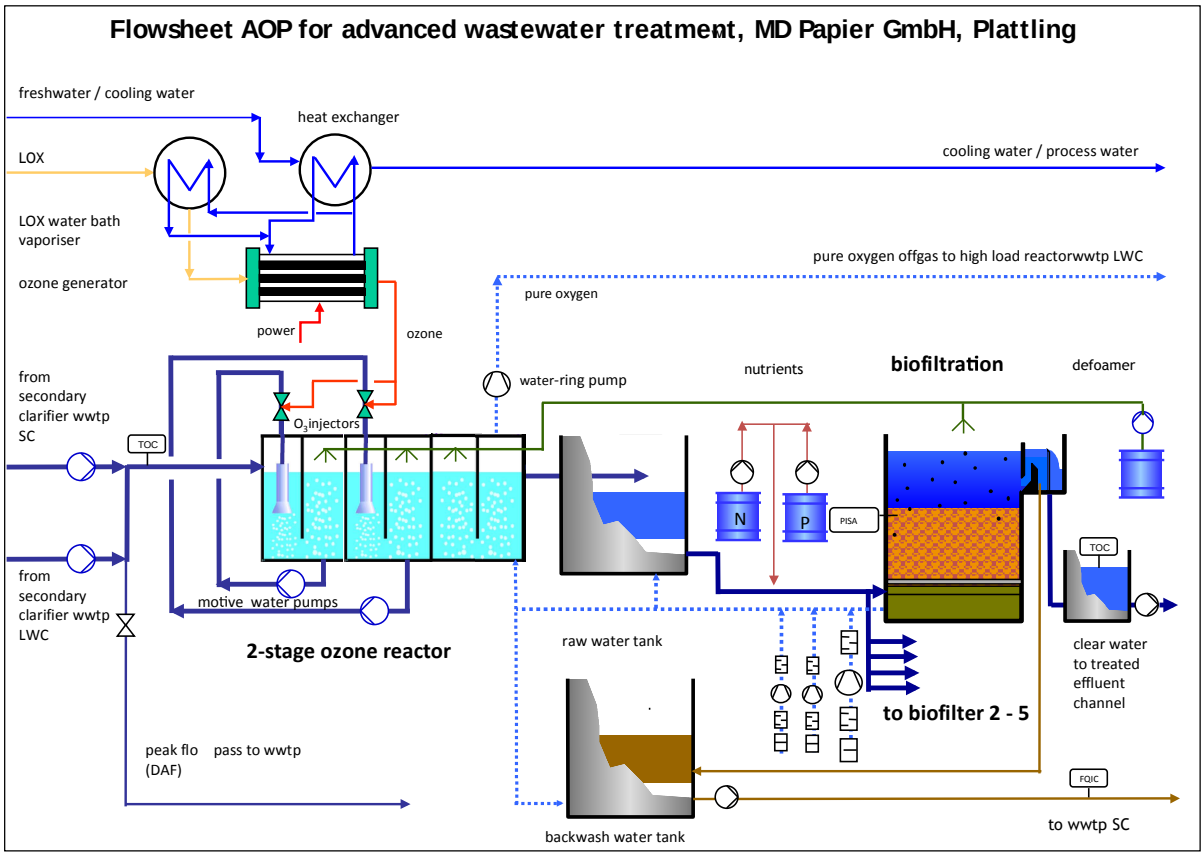

Figure 7: simplified flowsheet AOP at MD Papier GmbH, Plattling

This new process combination consists of a depressurized two-stage ozone reactor (as chemical oxidation stage) followed by five biological up-flow fixed bed biofilters (as biochemical oxidation stage). Only a small amount of biological excess sludge through advanced biodegradation (effect of partial oxidation with ozone) results from the regular backwash of the biofilters.

Dewatering is managed together with the biological excess sludge from the WWTP by implementation of an efficient pre-dewatering and belt filter dewatering press with reduced primary

sludge feed. The total separation of the far reduced tertiary sludge amount is then technically possible. This remaining small amount of tertiary sludge can be mixed with the primary sludge and dewatered in the existing screw presses without disturbing the operation of the presses.

The new applied ozonation in two serial ozone reactors equipped with an efficient ozone injection and distribution system are able to optimize the specific ozone consumption. Ozone production is controlled by TOC-online measurement devices in the inflow of the first ozone reactor and outflow of the biofilter.

2.5 Project targets

The optimization and extension measures are in accordance with the requirements stipulated by the Federal Environmental Agency (BMU) in the context of the Environment Innovations' Program.

The main project objectives are summarized below:

- Retention of a total specific COD discharge below 3.0 kg per tonne of paper in the total effluent by partial flow treatment and COD-removal control in the AOP (LWC or SC effluent to be treated) to ensure the preservation of the environmental quality of the receiving river Isar in a sensitive FFH area.

- Optimization of the specific ozone consumption; expected range after optimization 0.4 - 0.6 kg ozone per kg of COD eliminated (design is ≤ 1.0 kg O_3/kg $COD_{elim.}$).

- Further reduction of the specific energy consumption per kg of COD eliminated (reference value according to BREF is 20 kWh/kg $COD_{elim.}$).

- Improving the overall energy efficiency by optimization of the specific ozone consumption related to the COD to be eliminated.

- Operation of the existing DAF only under peak conditions to achieve a far reduced tertiary inorganic sludge amount in the existing DAF (the targeted reduction is more than $^2/_3$ of today's tertiary sludge amount of approx. 662 t/a) and to avoid the environmental disadvantages (increased salinity, inorganic sludge production with combined negative environmental effects during sludge treatment and utilisation).

- Production of scientific knowledge from additional measuring program for examination of the elimination of AOX, chelating agents (EDTA, DTPA), endocrine disruptors and micro pollutants e. g. bisphenol A by AOP.

3 Project implementation

3.1 Time plan

The implementation of the project “optimized ozone application for advanced wastewater treatment for the production of magazine paper” at MD Papier GmbH, Plattling, lasted 15 months. The AOP went into operation in August 2013, 12 months after construction began.

The statistical and graphical analysis to assess the performance and project objectives after commissioning took place during the period August 2013 until October 2014.

3.2 Basic design data AOP

The results of the statistical evaluation of the operation data outflow secondary biological treatment LWC-line and influent design data to the AOP are shown in Table 1 (based on 2-hour composite samples: statistical evaluation period January – September 2011).

For statistical data evaluation, we use the statistical parameters which are explained in the following: md = median of the available data or 50th percentile, mv = arithmetical mean value or average, s = standard deviation of a grab sample calculated for n-1, v = coefficient of variation or relative standard deviation, min = minimum (resp. lowest measured) value, max = maximum (resp. highest measured) value, mv+s corresponds nearly to 80th percentile (80% of the values are to be expected below this value) or exactly 83,5th percentile, mv+2s corresponds to 95th percentile, accordingly are to be understood mv-s as 20th percentile and mv-2s as 5th percentile, n = number of data evaluated or number of values in the grab sample.

Table 1: design data inflow AOP equals outflow of secondary clarifier after biological treatment

Design data AOP LWC line, MD Papier GmbH, Plattling					
description	**parameter**	**unit**	**mv**	**design**	**Statistical definition of the design data**
Total flow outflow WWTP LWC (equals outflow of secondary clarifier)					
daily flow rate	Q_d	m^3/d	10,490	14,400	mv + 2s
peak flow deduction (15 %)	Q_d	m^3/d		2,160	mv + 2s
design data inflow AOP					
daily flow rate	Q_d	m^3/d	10,490	12,240	mv + 2s
hourly flow rate	Q_h	m^3/h	437	510	mv + 2s
daily COD-load	$B_{d,COD}$	kg/d	3,577	4,865	mv + 2s
COD-concentration	COD	mg/l	341	397	mv + 2s
COD-concentration expected (setpoint)	COD	mg/l	290	290	max
COD-concentration to be eliminated	$COD_{elim.}$	mg/l	51	107	mv + 2s
daily COD-load to be eliminated	$B_{d,COD,\ elim.}$	kg/d	535	1,320	mv + 2s
BOD-concentration	BOD	mg/l	15	35	mv + 2s
N-inorganic concentration	N_{inorg}	mg/l	3.2	6.9	mv + 2s
P-total concentration	P_{tot}	mg/l	0.9	2.1	mv + 2s
AOX-concentration	AOX	mg/l	0.2	0.4	mv + 2s
suspended solids concentration	SS	mg/l	15	25	mv + 2s
temperature	T	℃	35	39	max
pH-value	pH	-		6.5 – 8.5	min – max

Table 1: It is foreseen that depending on the load either wastewater outflow secondary clarifier SC-line or outflow LWC-line can be treated in the AOP.

In addition it is possible that either a partial flow of untreated wastewater at the inlet of WWTP SC or WWTP LWC can be pumped to one or the another WWTP in order to compensate fluctuations in load.

The hydraulic daily capacity of the AOP is designed for 12,240 m³/d, which is comparable to approx. the 85-percentile value of the daily flow. The hydraulic continuous hourly flow is up to 510 m³/h. The biofiltration is always operated even if ozonation is not required.

The AOP is not designed to treat peak flows. An effluent flow above 510 m³/h can either be treated in the existing tertiary DAF of the SC-treatment line or flows directly

to the total effluent if the wastewater is low loaded. The capacity of the DAF is sufficient for the treatment of this supplementary limited flow.

The size of the ozone reactors (design parameter is the HRT) and the area of the biofilters (design parameter is the hydraulic surface load) can be optimized.

Due to a lack of nutrients in papermill effluent additional measures for nitrogen and phosphorous removal are not required. Usual dimensioning rules according to the German ATV / DVWK standards do not have not to be applied [ATV (2000].

3.3 Treated effluent quality outflow AOP

The design of the AOP is based on target values to be achieved in the treated effluent for different quality parameters as shown in Table 2.

Table 2**:** treated effluent quality outflow AOP

Treated effluent quality parameters outflow AOP, MD Papier GmbH, Plattling				
description	**para-meter**	**unit**	**design**	**statistical definition of the design data**
design data outflow AOP				
daily flow rate	Q_d	m^3/d	12.240	mv + 2s
hourly flow rate	Q_h	m^3/h	510	mv + 2s
daily COD-load to be eliminated	$B_{d,COD,\ elim.}$	kg/d	1,320	mv + 2s
COD-concentration selected	COD	mg/l	290	max
BOD-concentration	BOD	mg/l	20	mv + 2s
N-inorganic concentration	N_{inorg}	mg/l	8.0	mv + 2s
P-total concentration	P_{tot}	mg/l	1.5	mv + 2s
AOX-concentration*	AOX	mg/l	0.4	mv + 2s
total suspended solids concentration	TSS	mg/l	15	mv + 2s
temperature	T	℃	35	max
pH-value	pH	-	6.5 – 8.5	min – max

- All parameters are measured as homogenized 2 h composite sample except for AOX (measured as homogenized grab sample) DIN EN ISO methods (external laboratories)
- COD: DIN 38409 Teil 41 (H41)
- BOD_5: DIN EN 1899-1
- P_{total}: DIN EN 1189
- N: DIN 38405 D9-3
- AOX: DIN EN ISO 9562

UPM internal methods

- COD: Hach-Lange cuvette test
- BOD_5: WTW Oxitop
- P_{total}: Hach-Lange cuvette test
- $N_{inorg\ total}$: Hach-Lange cuvette test

The analyses methods are in compliance with the Annex 1 of the German wastewater regulations. Some parameters are analyses in equivalent methods such as rapid test. The results have to be regularly compared with results from standard testing. The laboratories are certified according to DIN ISO 9001 and 14001 standards.

3.4 Main design data AOP

The main design data of the AOP according to the basic design data and the required effluent quality (see Table 1 and Table 2) are shown in **Table 3**.

Table 3**:** Main design data AOP

Main design data AOP, MD Papier GmbH, Plattling			
description	**parameter**	**unit**	**design**
Ozone reactor (2-stage reactor unpressurised operation)			
volume ozone reactor 1	V_{R1}	m³	96
ozone input reactor 1	$B_{h,\ ozone}$	kg/h	0 - 30
volume ozone reactor 2	V_{R2}	m³	96
ozone input reactor 2	$B_{h,\ ozone}$	kg/h	0 - 30
operation mode reactor 1 and 2	-	-	serial
ozone generation capacity	$B_{h,\ ozone}$	kg/h	55
ozone concentration feed gas (LOX)	O_3	wt.-%	10
hydraulic retention time ozone reactors total	HRT	H	0.4
specific ozone consumption (kg ozone / kg COD elim.)	$b_{h,\ elim.}$	kg/kg	<1.0
specific ozone consumption (kg ozone / kg COD elim.) target value after optimization	$b_{h,\ elim.}$	kg/kg	0.4 – 0.6
spec. energy consumption ozone generation (cooling water 22 ℃)	$p_{spec.}$	kWh/kg	9.2
spec. energy consumption ozone diffusion system	$p_{spec.}$	kWh/kg	2.1
Biofiltration			
surface area total	A_{total}	m²	78
volume total	V_{total}	m³	234
no. of biofilters	no.	-	5
operation mode biofilters	-	-	parallel
hydraulic surface load	q_A	m³/m²*h	6.5
COD removal efficiency AOP	ηCOD	%	28
operation until backwash	t	H	24
backwash water total	$V_{d,\ total}$	m³/d	800
sludge production COD-removal	$B_{d,\ SS\text{-}COD}$	kg/d	510

Main design data AOP, MD Papier GmbH, Plattling			
description	**para-meter**	**unit**	**design**
sludge production SS-removal	$B_{d, SS}$	kg/d	160
sludge production total	$B_{d, slg. total}$	kg/d	670
spec. energy consumption biofiltration (incl. pumping station)	$p_{spec.}$	kWh/m^3	0.29
Nutrients			
BOD: Nitrogen: Phosphorous-ratio	BOD: N: P	-	100:5:1
daily BOD-load to be eliminated	$B_{d, BOD elim.}$	kg/d	630
urea (CH_4N_2O) 100 %	$B_{d, urea}$	kg/d	68
phosphoric acid (H_3PO_4) 80 %	$B_{d, H3PO4}$	kg/d	25
Defoamer			
defoamer (surface biofilters)	$Q_{d, defoamer}$	l/d	60

Note: Dosage of nutrients and defoamer is installed but will be used only if required.

3.5 Technical implementation AOP

3.5.1 Wastewater collection points for AOP

Wastewater to be treated in the AOP occurs at following points:

- Biological treated wastewater outflow secondary clarifier before DAF of SC-treatment line.
- Biological treated wastewater outflow secondary clarifiers of LWC-treatment line.

The tertiary treated effluent after DAF from the SC-treatment line flows by gravity usually directly to the main connecting channel to the river Isar.

The treated effluent outflow of secondary clarifier's LWC-treatment line is separated from the existing overflow tank to the main connecting channel to the Isar and is collected in new pump tanks. The existing overflow tank is now used as emergency overflow only.

The wastewater from the pump tanks is either pumped directly to the AOP or is passed to the DAF in cases of a peak flow.

The clear water after AOP treatment is pumped to the outflow channel after DAF and flows as mixed total effluent to the main connecting channel to the river Isar.

3.5.2 Overview of implemented technical measures as prerequisites for optimized AOP

Several optimization measures for compensation of the increased pollution loads and to achieve the best possible treatment results in terms of COD removal efficiency after secondary effluent treatment for a WWTP had to be developed and implemented within the existing WWTP.

The results of the technical concept studies showed that as a first step, cross-linking of the two existing wastewater treatment lines is required for a better compensation of shock loads.

Optimization measures for increased biological removal efficiency such as an increased filling degree with carrier material in the aerobic high load stages and an improved oxygen supply and control in the biological aerobic processes, avoidance of sludge thickening in the static thickeners, have to be applied in the existing WWTP in order to achieve the best possible treatment results before tertiary treatment.

The main effluent treatment measures for the technical and technological implementation of the AOP are:

- Increasing the filling degree with carrier media in the aerobic high load stages of the existing WWTP and improving oxygen supply and control to achieve the best possible biological removal efficiency before tertiary treatment.
- Installation of new pump tanks and pumping station outflow secondary clarifiers LWC-treatment line to AOP interconnecting pipe to the AOP with controlled peak flow pass.
- New pumping station outflow secondary clarifier SC-treatment line for the partial flow to AOP in order to achieve an economic operation for the elimination of persistent COD (decision to treat outflow secondary clarifier SC-treatment line instead of DAF) and a far reaching reduction of precipitation sludge (avoidance of cross-media effects).

  Note: the examination of differences in the characteristics of LWC- or SC-wastewater for AOP could not be studied in this project but is scheduled on a medium-term.
- Installation of two new TOC-online measurement devices for control and automation of the effluent of the secondary treatment to be treated by AOP.
- Installation of an automatic back flushing filter for separation of coarse solids from inflow AOP

- Installation of an ozone generator with a capacity of 55 kg/h ozone from LOX as carrier gas.
- Installation of two-stage modular ozone reactors with individually controllable ozone diffuser systems.
- Fitting the ozone reactors each with injector/diffuser system as depressurised reaction chamber at high efficient counter current flow with extended retention time for chemical reaction with slow kinetics.
- Reuse of the pure oxygen offgas from the ozone reactors for additional oxygen supply in the high-load moving bed bioreactors of the WWTP LWC line after recompressing in water-ring pumps (partial substitution of the oxygen supply from compressed air production of the existing compressors).
- Energy recovery through freshwater use as cooling water in the secondary cooling water circuit for indirect cooling of the ozone generator, cooling water circuit and further use of the preheated cooling water as process water in the production.
- Additional energy recovery through an indirect additional cooling water circuit for evaporation of the LOX in water bath vaporisers in the primary cooling circuit of the ozone generator.
- Installation of 5 parallel operated modular up flow fixed bed aerated biofilters.
- Ensuring a far reaching automation of the process controlled by an online flow and TOC measurement to optimize the load depending ozone production.
- Cross-linked operation of the WWTP SC and LWC for balance of capacity reserves depending on the production capacity of the SC and LWC production lines.
- Installation of an improved sludge dewatering with a pre-dewatering / belt filter press cascade after far reduced tertiary sludge and reduced primary sludge addition
- Increasing the removal of thin biological excess sludge from the secondary clarifiers instead of static thickeners and improved MLSS adjustment for continuous sludge load control in the activated sludge basin and best possible COD removal efficiency in the secondary treatment before AOP

The implemented technical optimization measures and the cross-linked operation of the WWTP is shown schematically in **Figure 8**.

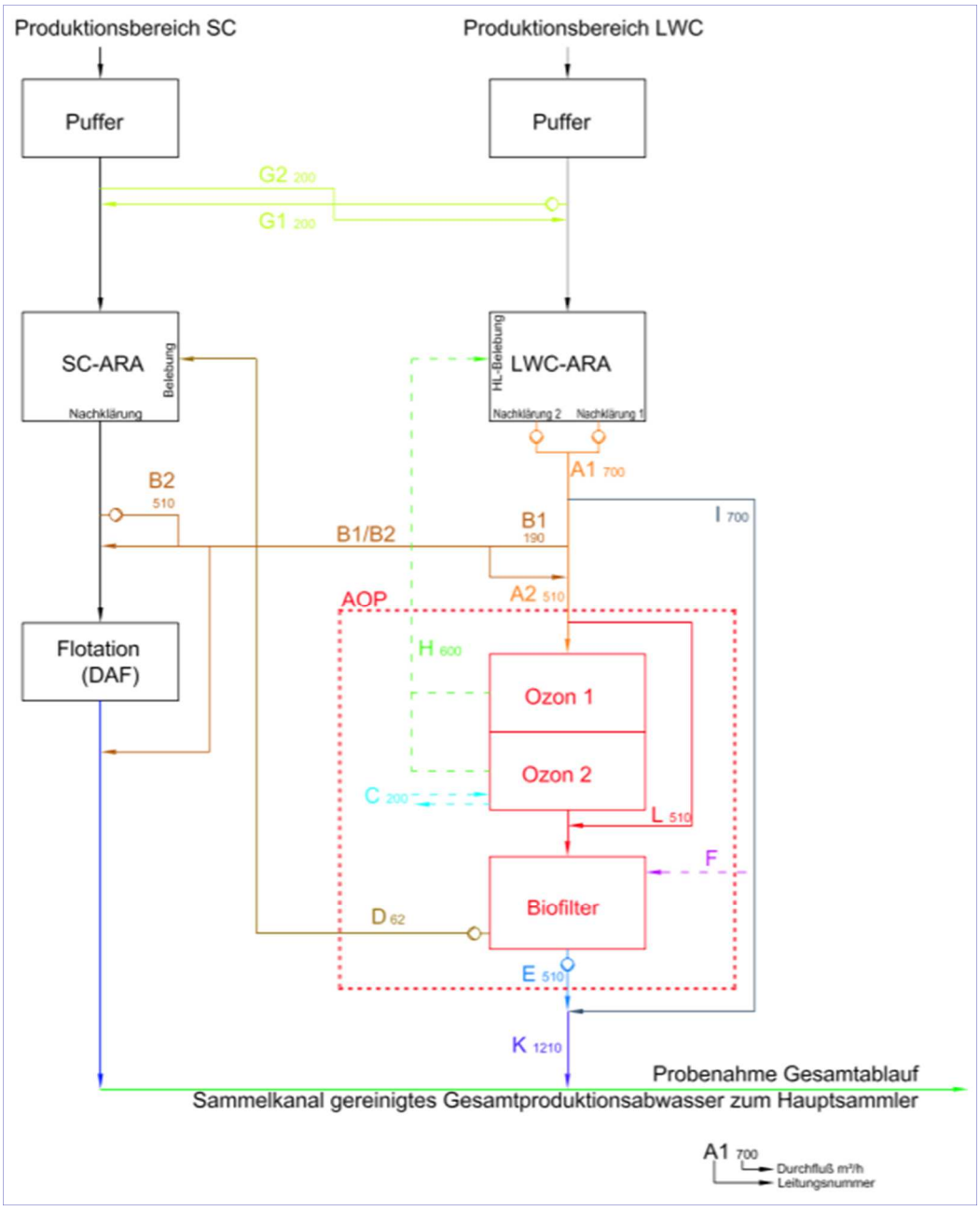

Figure 8: schematic simplified block diagram AOP with cross-linked operation WWTPs, MD Papier GmbH, Plattling

Abbreviations used in Figure 8:

- No.	Position	Medium
- A1/2	outflow secondary clarifier WWTP LWC to AOP	wastewater
- B1/2	connection LWC to DAF / outflow secondary clarifier WWTP SC to AOP	wastewater
- C	cooling water	freshwater
- D	backwash water biofilter	excess sludge
- E	clearwater AOP to main outflow channel	wastewater
- F	dosing pipe nutrients urea, H_3PO_4	nutrients
- G1/2	raw water compensation SC to LWC, LWC to SC	wastewater
- H	off gas ozone reactor (pure oxygen)	carrier gas (LOX)
- I	by-pass AOP	wastewater
- K	total effluent to main channel	wastewater
- L	by-pass ozone reactor	wastewater

Besides the optimization measures as described above the existing WWTPs are operated optimized but without modifications such as extended or new basins within the WWTP (except the pump tanks).

The layout of the AOP and its integration in the existing WWTPs with new pumping stations and interconnecting pipes is shown in **Figure 9**.

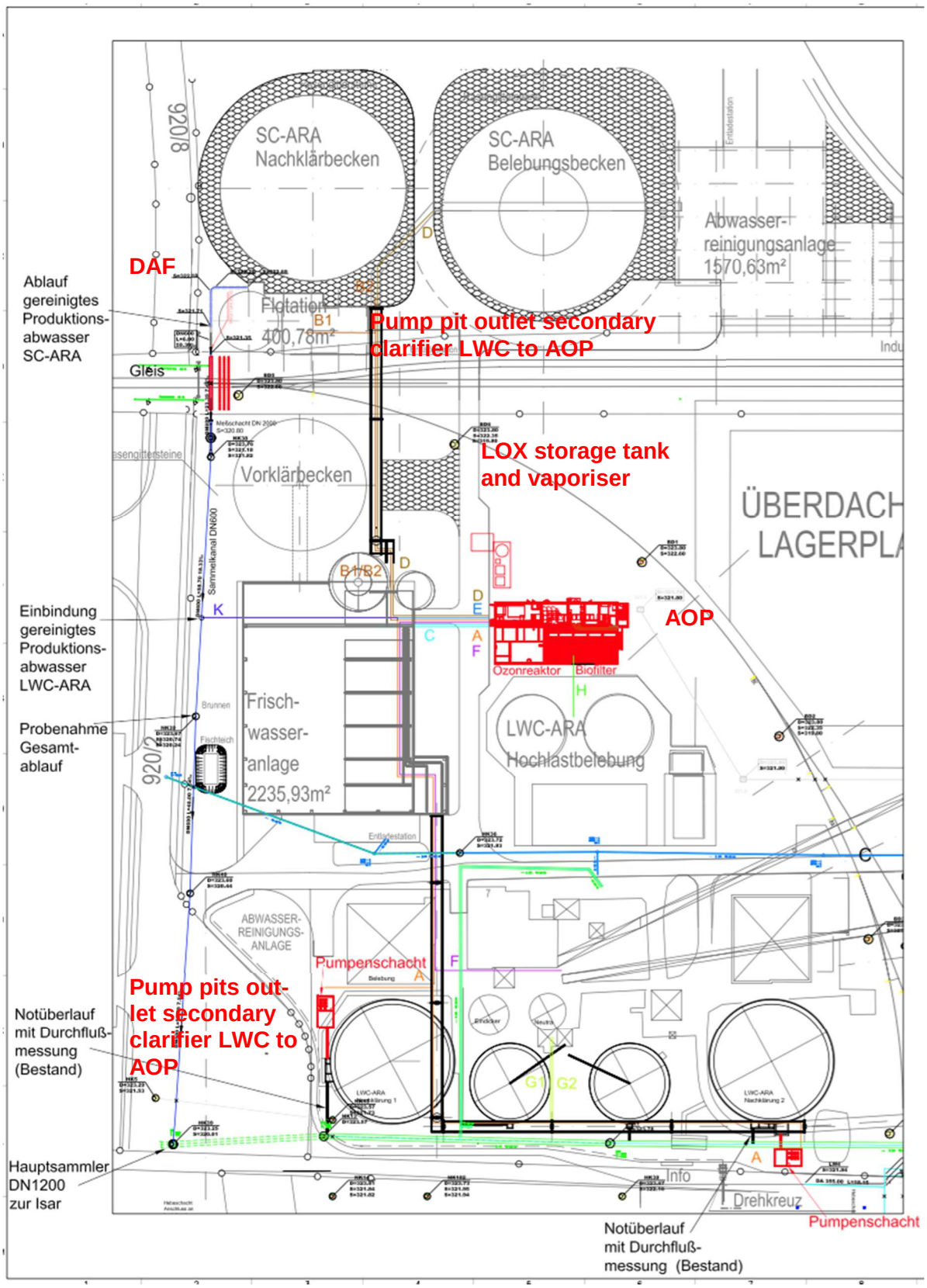

Figure 9: layout AOP (extensions are marked in red)

3.6 Process stages according to the AOP design

The individual process stages are described briefly below:

3.6.1 New pumping stations to AOP

The full biologically treated effluent from the outflow of the secondary clarifiers LWC-treatment line is collected in new pump tanks and is mainly pumped in full stream to the AOP. The additional flow during peak flow conditions above 510 m^3/h is passed to the DAF of SC-treatment line or directly to the outflow of the DAF for discharge of the mixed total effluent.

If the LWC effluent is low loaded, so that additional AOP treatment is not required, the secondary treated effluent from the outflow of the secondary clarifier SC-treatment line is pumped via a new pumping station to the AOP accordingly, to avoid precipitation treatment in this line.

Flow meters are installed in each pipe to the AOP and in the outflow as well as in the total effluent.

3.6.2 TOC-online measurement for ozone generation AOP

TOC-online measurement devices are installed for continuous control of the TOC-concentration at the in- and outflow of the AOP and for quality control of the total effluent. The COD-concentration is calculated with an average COD/TOC-ratio factor.

Currently the operator starts the ozone stage manually. Set points are the TOC inflow and outflow online values and the average COD/TOC-ratio, which is determined by evaluation of the operation data. The COD setpoint which has to be achieved in the outlet of the AOP, is 290 mg/l. The ozone production is calculated by the COD-load to be eliminated and the specific ozone consumption (kg ozone per kg COD eliminated).

In future it is planned that online load calculations for the in- and outflow to the AOP as well as in the total effluent are linked and automated to achieve a load depending optimized ozone production. More operational experience is required before a full automation mode can be implemented in the process control system.

3.6.3 Automatic back flushing filter

An automatic back flushing filter for separation of coarse solids is installed at the inflow of the AOP as a security filter.

The back flushed screening residue flows to the backwash water basin of the biofilters and is pumped back to the aeration basin of the WWTP SC line. The coarse solids from the automatic back flushing filter are expected to be low after secondary clarification (coarse solids

should be removed upstream of the WWTP). The solids are removed with the excess sludge from secondary clarifier.

3.6.4 Liquid oxygen (LOX) storage tank with water bath vaporiser

The required gaseous oxygen for the ozone production is supplied from a liquid oxygen (LOX) storage tank delivered on demand by truck from a gas supplier (Figure 10).

Figure 10: LOX storage tank with water bath vaporiser

LOX is evaporated in a special LOX water bath vaporiser instead of classical air vaporiser systems. The LOX water bath vaporiser is directly connected with a closed cooling water circuit to the ozone generator. The cooling energy for the LOX evaporation is again reused for cooling the ozone generator (see more information in the following). An air vaporiser is installed as a stand-by for LOX evaporation for security only.

The LOX tank is located outdoor near the AOP building.

3.6.5 Ozone generation

Ozone is generated in the ozone generation unit. The main components of the ozone generation unit are the ozone generator and the power supply unit.

The ozone generator consists of a horizontal cylindrical reaction vessel with diverse flange connections for the carrier gas (pure oxygen) and product gas (pure oxygen plus about 10-% wt. ozone gas) and the cooling water connections. A specific number of stainless-steel pipes are welded between the end plates of the vessel. These pipes are operated as earth electrodes. The cooling water circulates around the pipes and dissipates the released heat of reaction. Cooling water pipes connected outside the end plates of the vessel enable the cooling water exchange (see **Figure 11**).

Figure 11: ozone generator AOP

Dielectrics consisting of special coated stainless steel bodies are fixed inside the stainless steel pipes and are working as high voltage electrodes.

The principle of the ozone production in the ozone generator unit can be described simplified as follows:

The feed gas flows into the tight annular gap between dielectrics and the cooled stainless steel pipe. Ozone molecules are formed when oxygen molecules are decomposed by the energy input through „silent electrical discharge“.

The production of ozone with the use of pure oxygen as a carrier gas is shown in **Figure 12** as a simplified schematic drawing.

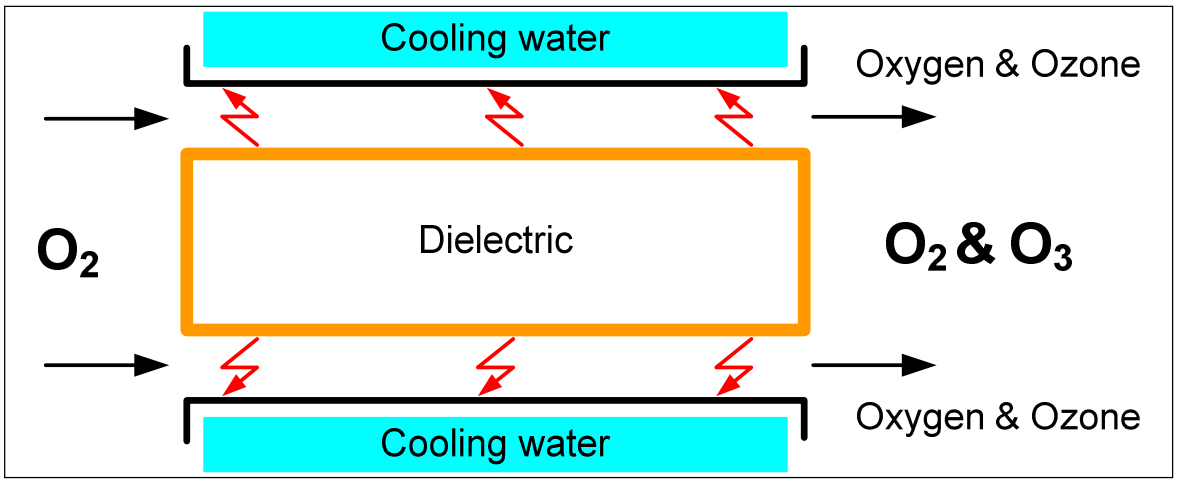

Figure 12: schematic drawing of the ozone production

3.6.6 Cooling water system

The reaction energy, which is not required for the generation of ozone, is led away with the cooling water. Cooling of the ozone generator is an essential factor for an efficient ozone generation. The inflow temperature of the cooling water is an important criterion for the efficiency of the ozone production. The inflow cooling water temperature can range between 5 ℃ to 30 ℃ whereas the lower temperature provides a better efficiency. A higher temperature restricts the ozone production.

The released heat of the reaction is dissipated by a heat exchanger. Freshwater produced on site as process water for the papermill is used as cooling water and is led back as pre-heated process water to the process water supply pipe to the papermill.

3.6.7 Depressurized 2-stage ozone reactor

The ozone reactors are designed as two stage modular ozone reactors with individually controlled diffuser systems. Each ozone reactor consists of diffusion and reactor chamber at high efficient counter current flow with extended retention time in the reaction chamber especially for chemical reaction with slow kinetics.

The water flow through each reactor is led by separating walls in each reactor so that the hydraulic retention time can be ensured and short cut circuits are avoided. The wastewater flow through each diffusion chamber is down flow whereas the feed gas with the ozone is distributed via the ozone injection and diffusor system as an up flow bubble column in counter current to the wastewater.

The ozone reactors are operated under depressurised conditions (compared to the design in one ozone reactor, which is operated under pressurised conditions of several bar). The predominant reaction principle is an intensive „ gas-to-liquid interface“ reaction.

A range of approx. 0 – 70 % of carrier gas (with ozone) can individually be distributed via automatic control valves into each reactor.

The objective is the accumulation of biodegradable compounds with a minimised quantity of ozone and the avoidance of a further chemical oxidation of these substances (and an increased consumption of ozone). The biodegradation efficiency in the biofiltration stage is kept in an optimal range as well. An ozone consumption above or below the optimal level related to the wastewater matrix and the reaction kinetics of the soluble wastewater compounds shall be avoided.

The depressurised ozone reactor concept with ozone injection and diffusion system is schematically shown in **Figure 13**.

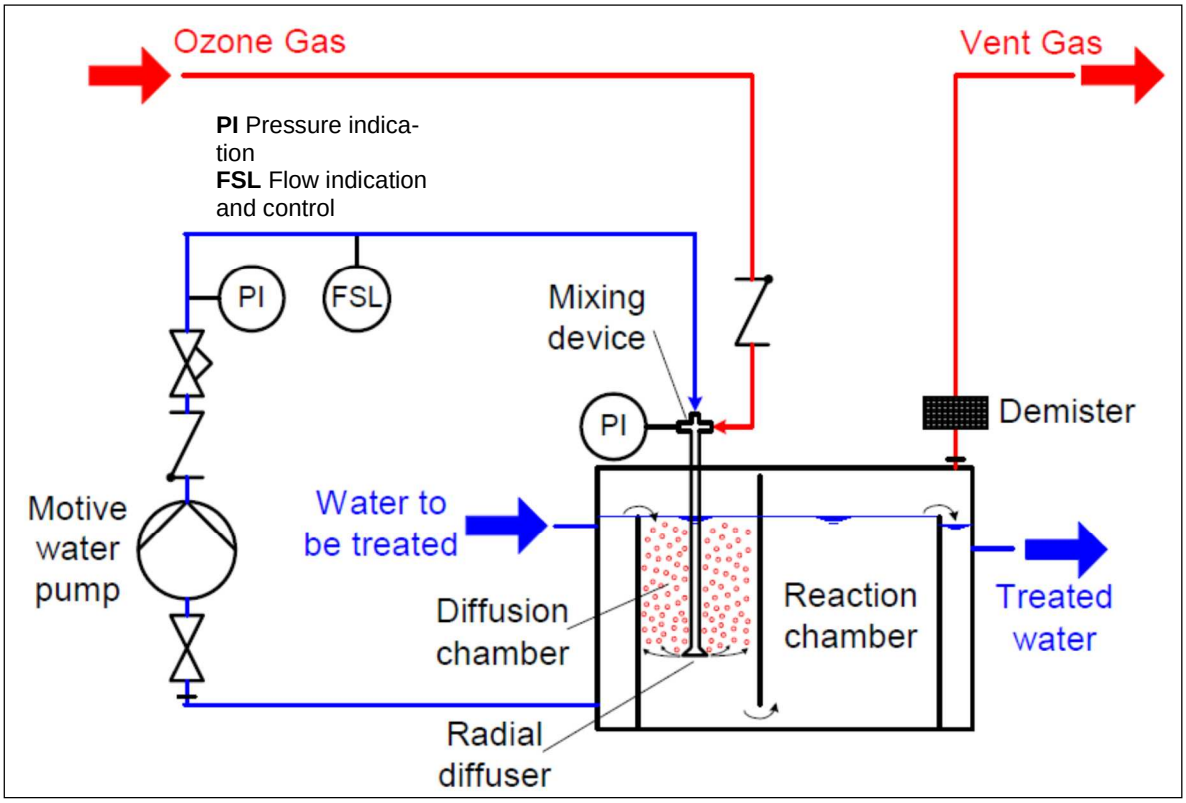

Figure 13: schematic flow diagram depressurised ozone reactor with special diffusion system and counter current bubble column (one reactor is shown)

3.6.8 Ozone injection and diffusion system

The influent is either pumped from the LWC or SC pumping station to ozone reactor one of AOP. The water flow through the AOP is by gravity.

Each ozone reactor is equipped with a motive water pump, injector and a special ozone diffusor system.

The motive water pumps generate an internal circulation flow. The carrier gas from the LOX vaporiser is injected in the mixing devices and is intensively mixed. The two phase gas / liquid system distributed by the ozone diffusion system and flows as a fine distributed bubble column counter current to the wastewater through the ozone diffusion chamber.

The view of the ozone injection and motive water pump of ozone reactor two is shown in **Figure 14**. The system is identically constructed as reactor one.

Figure 14: ozone injection and motive water pumps ozone reactor two AOP

The ozone concentration is measured online before further compression.

3.6.9 Ozone reactor offgas compressors

The off gas, which consists of more than 99 % pure oxygen (ozone loss is less than 1 %) is collected above the water level of the depressurized sealed reactor. The off gas is compressed by two water ring compressors (one stand-by) and is used for additional oxygen supply in the aerobic high loaded stage of the WWTP LWC line (Figure 15).

Figure 15: Ozone reactor offgas compressor

Excess ozone that might be contained in the off gas is immediately consumed in the high loaded stage due to the high concentration of suspended solids. Disadvantages to the biocenosis are not expected. According to diverse publications filamentous microorganisms can be reduced which even stabilises the high loaded reactor (and the activated sludge system as well) [Ried, Stapel, Koll (2002)], [Heinzle, Geiger, Fahmy, Kut (1992)].

A leakage of ozone into the atmosphere is not possible due to the gas-tight design according to the technical standards.

The wastewater after the second ozone reactor flows by gravity to an intermediate tank before further distribution to the biofilters. The reaction chambers and the final intermediate tank provide an additional reaction time. However, ozone is quantitatively consumed before the further biodegradation in the down flow biofilters.

The intermediate tank is designed to buffer a specified water volume, which is used for the backwash of the biofilters. Control valves and flow meters at the inflow of each biofilter achieve the equal distribution outflow from the intermediate tank to the biofilters.

During times of low concentration and low load the ozone reactors are either continually passed through without ozonation or can be bypassed.

The biofilters are always in operation.

3.6.10 Biofiltration

Transformed biodegradable organic compounds in the ozone reactors lead to an increase of the BOD concentration (expected BOD concentration below 100 mg/l after ozonation in the applied AOP process).

For low BOD concentrations wastewater biofilters that are widely used in papermill wastewater treatment are applicable. The biofilter reactor is a biological submerged filter containing a fixed, dense granular bed with influent wastewater flowing in an upward direction.

The system uses granulated burned clay (lightweight expanded clay aggregate) as a filter medium (biomass carrier) which serves as a biological contactor as well as a filter medium, eliminating the need for separate clarification.

Five biofilters each with a surface area of approx. 16 m^2 are in operation.

Biofilters in operation are shown in **Figure 16**.

Figure 16**:** aerated surface of the biofilter

The filters are aerated with compressed air from air blowers for oxygen supply of the fixed film biomass. The growth of biofilm by the biodegradation of the organic compounds (biological excess sludge) is controlled by backwash of the biofilters.

An adopted backwash program automatically initiates the backwash of the biofilters. Backwash of each biofilter is using backwash water and compressed air from a separate blower once per day. As backwash water the regular inflow and additional water volume in the intermediate basin is used.

The backwash water is stored and equalised in the backwash water basin and is continuously pumped back to the inflow of the activated sludge tank of the WWTP SC line. The small amount of biomass is removed with the excess sludge of the secondary clarifier and is pumped to sludge dewatering.

A view of the biofilter filter gallery and process air blowers besides the filter basins is shown in **Figure 17**.

Figure 17: Filter gallery biofilter AOP

As previously mentioned the biofilters are always in operation. The COD removal efficiency in the tertiary biofilters without ozonation lies typically in the range of approx. 10 – 15 %. The COD removal efficiency of the AOP (chemical plus biochemical oxidation) is designed to reach up to approx. 30 % during regular operation.

3.6.11 Chemical storage and dosing systems

3.6.11.1 Nutrients

For an optimal BOD and COD removal efficiency in the WWTP SC line and LWC line a sufficient nutrient supply with nitrogen (N-H_4 from Urea) and phosphorous (H_3PO_4 from phosphoric acid) is very important. A sufficient amount of nutrients is ensured if the N-NH_4 and P-

PO_4 at outflow of the secondary clarifiers are in the concentration range of 0.5 – 1.0 mg/l. Under these conditions the nutrient supply in the tertiary biofilters is sufficient for the long-term biofilm biocenosis. If the BOD concentration and load is increased when ozonation is required an additional dosing of nutrients might be necessary.

The possibility for an additional dosing of nutrients at the inflow to the biofilters is therefore installed. Additional dosing pumps are installed to ensure the nutrient supply in the biofilters when required.

3.6.11.2 Defoamer

Defoamer dosing from IBC containers in case of foam development above the water surface of the ozone reactors and above the surface of the biofilters have been installed. Primarily clear water is used as spray water and distributed with nozzles above the surface. Additional defoamer is dosed only when required. The use of defoamer is not related to the AOP and is used only if the wastewater contains surface-active substances from the production.

The defoamer IBC container is installed in the operation building of the AOP.

3.7 Optimized sludge dewatering concept

General information

A usual sludge treatment system consists mostly of an aerated sludge buffer if sludge storage is required and sludge dewatering using either centrifuges or belt filter presses. Depending on the sludge concentration a pre-thickening machine is required before the real sludge dewatering either with a centrifuge or with a belt filter press can be applied. Drum thickeners, disc filters or gravity tables are often used for the pre-thickening of the thin excess sludge out of the secondary clarifiers of activated sludge systems.

Centrifuges require usually a sludge concentration for dewatering typically above 0.9 % dry matters, belt filter presses typically above 3.0 %.

The sludge dewatering with centrifuges requires usually a specific polymer dosage of 15 – 20 g polymer per kg sludge as dry matter, belt filter presses 4 – 7 g polymer per kg sludge as dry matter. Centrifuges require far more electrical energy but need less manpower for operation and maintenance.

The dryness of biological excess sludge alone can be expected to reach 18 – 25 % as dry matter. Biological excess sludge from WWTP in papermills is different from municipal excess sludge where different processes are applied e. g. aerobic or anaerobic sludge stabilisation

with denitrification and phosphorous removal which is not applicable for pulp and paper wastewater (see chapter 3.6.11.1, nutrients).

Mixing and adding primary sludge to the biological excess sludge increase dry matter content by the amount of fibers and ash from the primary sludge.

Improved sludge dewatering concept:

The thin sludge is thickened in an efficient new pre-dewatering machine as a gravity table, which is directly connected to a high-pressure belt filter press. Less cross-media effects due to less polymer consumption and less energy consumption and some flexibility concerning changes in the excess sludge characteristics are expected with this concept (e.g. a program for further reduction of fiber and ash losses in the production is in progress which will influence the dewatering characteristics in a certain way). However, predictions about the expected excess sludge properties are difficult to make in advance. In other cases other concepts might be more advantageous.

The addition and mixing of much less primary sludge into the feed tank is foreseen (approx. 15 – 25 % compared to 40 -50 % previously) while a dry matter content of approx. 30 % can be achieved.

As described in chapter 3.6.10, the comparatively small amount of biological excess sludge from the biofilters is dewatered together with excess sludge of the WWTP.

The substantially reduced remaining tertiary sludge can now be mixed with the primary sludge from the primary clarifiers and is dewatered with the existing screw presses.

As described in chapter 2.4.2, the optimized excess sludge-dewatering concept enables a total bypass of the existing static sludge thickeners and the removal of excess sludge directly from the return sludge circuit leaving the secondary clarifier (much less hydraulic retention time of the excess sludge before sludge dewatering, a far less chargeback from the filtrates of the sludge presses and less odour results).

The pre-thickener and high pressure belt filter press is shown in **Figure 18**.

Figure 18: pre-thickener and high pressure belt filter press

3.8 Process Monitoring

The sampling points for operation control and self-monitoring for the WWTP and implemented AOP are summarised as follows:

- P1: Outflow secondary clarifier 1 WWTP LWC line
- P2: Outflow secondary clarifier 2 WWTP LWC line
- (P1 + P2: is adequate to the total effluent WWTP LWC line)
- P3: Outflow biofiltration AOP
- P4: Outflow secondary clarifier WWTP SC line
- P5: Outflow DAF WWTP SC line
- P6: Total outflow before discharge (WWTP LWC mixed with WWTP SC)

The method and frequency of the analyses for the process monitoring are shown in **Table 4** and **Table 5**.

Table 4**:** Method and frequency for process monitoring WWTP

location	**control parameter**	**dimension**	**frequency**
Functional control	Function of all main systems		d (daily)
Outflow secondary clarifiers (P1, P2, P4)	Q_d	m^3/d	c (continu-ously)
	t	°C	c
	pH	-	c
	sS	mg/l	d
	COD	mg/l	d
	BOD_5	mg/l	w (weekly)
	$N_{inorganic}$ (NH_4+NO_3+NO_2)	mg/l	d
	P_{total}	mg/l	d
	AOX	mg/l	2 w
	TOC	mg/l	c
Outflow DAF und AOP (P3, P5)	t	℃	c
	pH	-	c
	COD	mg/l	d
	BOD_5	mg/l	w
	$N_{inorganic}$ (NH_4+NO_3+NO_2)	mg/l	w
	P_{total}	mg/l	w
	TOC	mg/l	c

Table 4**:** P1 – P6 are equipped with automatic sampling devices (flow proportional 24 h and / or 2 h composite samples).

The samples inflow AOP, outflow ozonation and outflow AOP are taken with a time delay of one hour for each stage. Since the beginning of May 2014 the outflow AOP has been additionally measured by a new automatic sampling device (24 h composite samples). Since then, the efficiency calculations inflow and outflow AOP are performed by adding the 24 h composite samples (24 h composite samples P1, P2, P4 and P3). This provides more consistent values because the ozone consumption is always tapped as a 24 h consumption value. The removal efficiency calculations for the individual AOP stages are carried out by grab samples.

The flow of the partial streams is measured with inductive flow meters. Temperature and pH in the total effluent are measured online.

TOC is automatically measured in online TOC-analyzers between inflow and outflow of the AOP.

All online data are collected in the process control system.

The parameters for the official control and self-monitoring of the total mixed effluent from the SC and LWC WWTP lines before discharge are shown in **Table 5**.

Table 5: Method and frequency for process monitoring WWTP total effluent

location	control parameter	dimension	frequency
Quality control total effluent (P6)	t	℃	c (continously)
	pH	-	c
	COD	mg/l	d (daily)
	BOD_5	mg/l	w
	$N_{inorganic}$ (NH_4+NO_3+NO_2)	mg/l	d
	P_{total}	mg/l	d
	AOX	mg/l	m (monthly)

Table 5: The total outflow of the mixed effluent after DAF and new AOP is monitored from the homogenised 2 h composite sample.

The parameters in Table 4 and **Table 5** are measured to operate the WWTP and perform quality control checks of the total effluent before discharge as well as of the partial flows. All control parameters except AOX are measured in the papermill's laboratories.

Analyses and measurement results, operation and maintenance activities are all documented in the operational logbook.

The methods are in compliance with the appendix 1 of the German Wastewater Ordinance. Some parameters are analyzed with equivalent methods such as rapid tests. The laboratories are certified according to DIN ISO 9001 and 14001 standards.

3.9 Additional monitoring program

The program is based on the PTS-FORSCHUNGSBERICHT IGF 16552. Theme: *Studies on reducing organic trace compounds in paper industry effluents with the help of advanced treatment technologies*. The following trace substances or species were studied in this project: chelating agents, phthalates, bisphenol A (BPA), polycyclic aromatic hydrocarbons (PAHs), chlorinated aromatic hydrocarbons (CAHs) and poly- and perfluorinated compounds (PFCs). The concentrations of these substances were close to or below the detection limit in all real samples tested.

Advanced oxidation processes (AOP) have shown some good results.

The idea was to verify the elimination with AOP under industrial conditions.

Because the concentrations of these substances were close to or below the detection limit, some chemicals have been added to the paper wastewater during the trials.

The additional measuring program, as agreed upon with the Federal Environmental Agency (UBA) in the context of the Environment Innovations' Program, is summarized in **Table 6** and Table 7.

Table 6**:** Overview measuring program

Overview measuring program project *optimized ozone application for advanced wastewater treatment from production of magazine paper*							
Performing company: MD Papier GmbH, Plattling; Meeting dated 27-01-2014, participants: Mrs. Almut Reichart (UBA), Messrs. Wolfgang Haase (MD Papier), Alfred Helble (CM Consult) Objective: Determination of the measuring program and supervision by UBA							
Measures	**Parameter**	**Sampling points**	**Type of sampling**	**Frequency and number of tests**	**Duration**	**Laboratories**	**Remarks**
1. Test for optimization of the ozone consumption AOP - Tests for different distribution of ozone and efficiency - TOC controlled process control of ozone generation and diffusion	COD, BOD, TOC COD/TOC, BOD/COD spec. ozone consumption TOC	Inflow AOP Outflow reactor 1 Outflow reactor 2 In-/outflow AOP	24 h composite sample (CS), Grab sample Grab sample Grab sample 24 h CS, Grab sample TOC-Online	ongoing approx. 6 days for test ongoing	Feb. - Sep. 2014	Lab MD Lab MD Lab MD Lab MD Lab MD	- wastewater load depends on the production; target is to examine periods with high loads and concentration - alternatively selected days with indicative conditions are chosen for test
2. Tests for analyses of specific wastewater parameters - Analyses of production spec. parameters and its elimination in the individual treatment stages WWTP and AOP	COD, TOC, AOX, chelating agents	Inflow AOP Outflow reactor 2 Outflow AOP	Grab sample Grab sample Grab sample	approx. 3 test days	Feb. - July 2014	Lab MD Synlab Synlab	- for AOX different sample treatment methods are uses
3. Analyses of micro pollutants - Analyses of micro pollutants and its elimination in the individual treatment stages WWTP and AOP	BisphenolA Phthalate, PAK, PFC (PFOS, PFOA)	Mech. pulp, raw effluent outflow WWTP (sec. clarifier inflow AOP) outflow ozone reactor	Grab samples sampling over 2 days	approx. 2 - 3 test series	Feb. - July 2014	IfP TU Darmstadt	- the number, sampling places, test series is determined after the first orientation tests
4. Endocrine disruptors - Analyses of endocrine disruptors in- and outflow AOP	Endocrine disruption (R-YEA-Test (modified yeast cells)	Outflow WWTP (Inflow AOP) Outflow ozone reactor Outflow AOP	Grab samples sampling over 2 days	approx. 2 - 3 test series	Feb. - July 2014	IfP TU Darmstadt	- the number, sampling places, test series is determined after the first orientation tests
5. Special tests - Ozone diffusion performance test: test for evaluation of the specific ozone diffusion capacity of the installed ozone diffusion system with the full decolorisation method using indigo blue - large scale batch test: analyses of the elimination of Bisphenol A / Phthalate in the wastewater and total oxidation with ozone	COD Color Ozone consumption, Bisphenol A, Phthalate, COD	Batch test Ozone reactor 1	Grab sample Grab sample Grab sample Grab sample Grab sample	approx. two 2 test days 1 test serie	March - May 2014 March - May 2014	TU München IfP TU Darmstadt Lab MD	- test organised in spring weather related - test with micro pollutants by addition only little above the detection limits according to existing published results or after additional lab test when required

An overview of the applied measuring methods is shown in Table 7.

Table 7**:** Overview measuring methods

Parameter	Method
TOC	Hach-Lange online analysator (Ozone digestion, IR spectroscopy)
COD	Hach-Lange cuvette test
BOD_5	WTW Oxitop
AOX	DIN EN ISO 9562
EDTA, DTPA	DIN 38413 – 8 (HPLC / UV-VIS))
Bisphenol A	Stir Bar Sorptive Extraction, GC / MS
Phtalates	GC / MS
Perfluorinated Compounds (PFC)	HPLC MS / MS
Polycyclic aromatic hydrocarbon (PAH)	Stir Bar Sorptive Extraction, GC / MS

4 Results

The operation data collated during the period between August 2013 and the start of October 2014 have been recorded and statistically evaluated.

The additional measuring program as agreed upon with Federal Environmental Agency (UBA) was executed between August and October 2014.

The evaluation results are presented in the following chapters.

4.1 Evaluation of the data monitoring

4.1.1 Statistical data evaluation AOP

The results of the statistical data evaluation August 2013 until October 2014 are shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** - Annex 1, Table 5

(See interpretation and discussion of the results in connection with chapter 4.1.2 graphical evaluation).

The results of the graphical evaluation of the operation data for the period August 2013 until October 2014 are shown in the following charts and graphical evaluation.

4.1.2 Charts and graphical evaluation

The ozone utilisation in the ozone reactors of the AOP is shown in **Figure 19**.

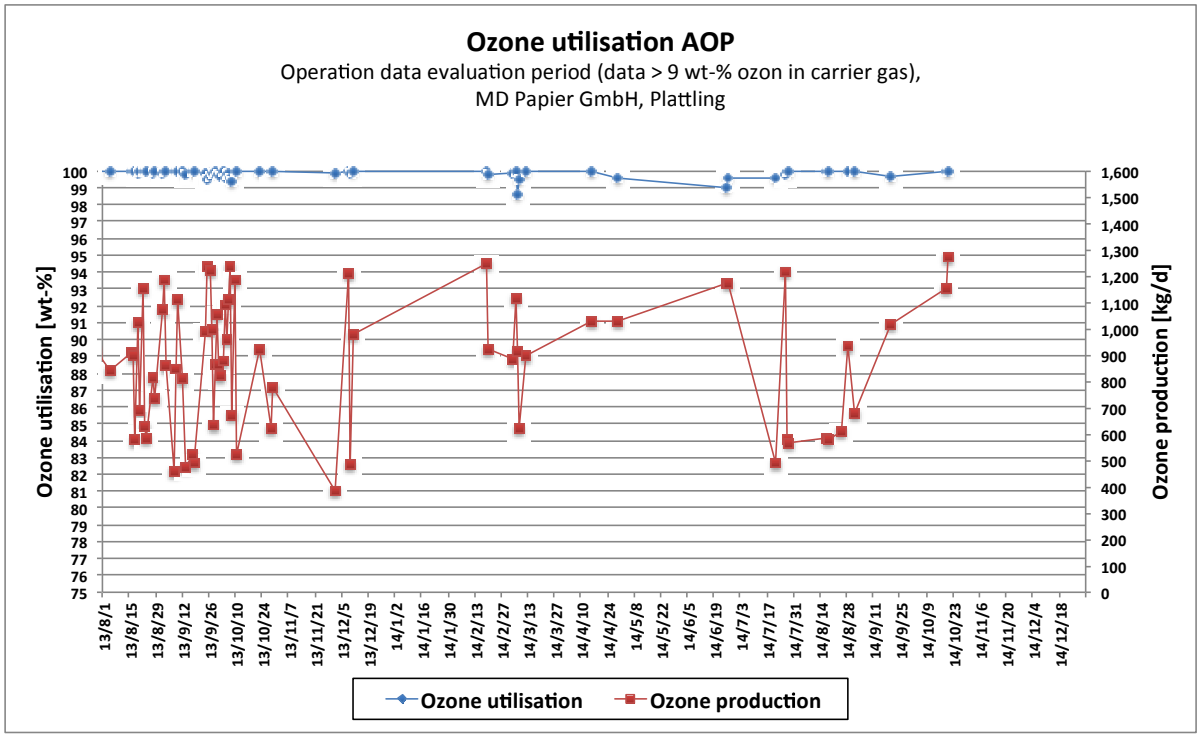

Figure 19: Ozone utilisation in ozone reactors AOP

The ozone concentration is measured with an ozone measurement device prior to the offgas compressor. The offgas compressor runs continuously with a flow capacity of 730 Nm^3/d. The product of flow and concentration results in the loss of ozone (kg/d). The total ozone generation is continuously measured and provided by the plc (kg/d). The loss (respectively the utilization) results as the ratio of utilization (1 minus loss divided through the total ozone production in per cent).

Figure 19 shows the almost complete ozone utilisation in the system. The statistical calculated average value is 99.9 %. The injection / diffusor system is very effective and fulfils the expectations of the two-stage concept.

The development of the inflow and outflow COD concentration in the AOP is shown in **Figure 20**.

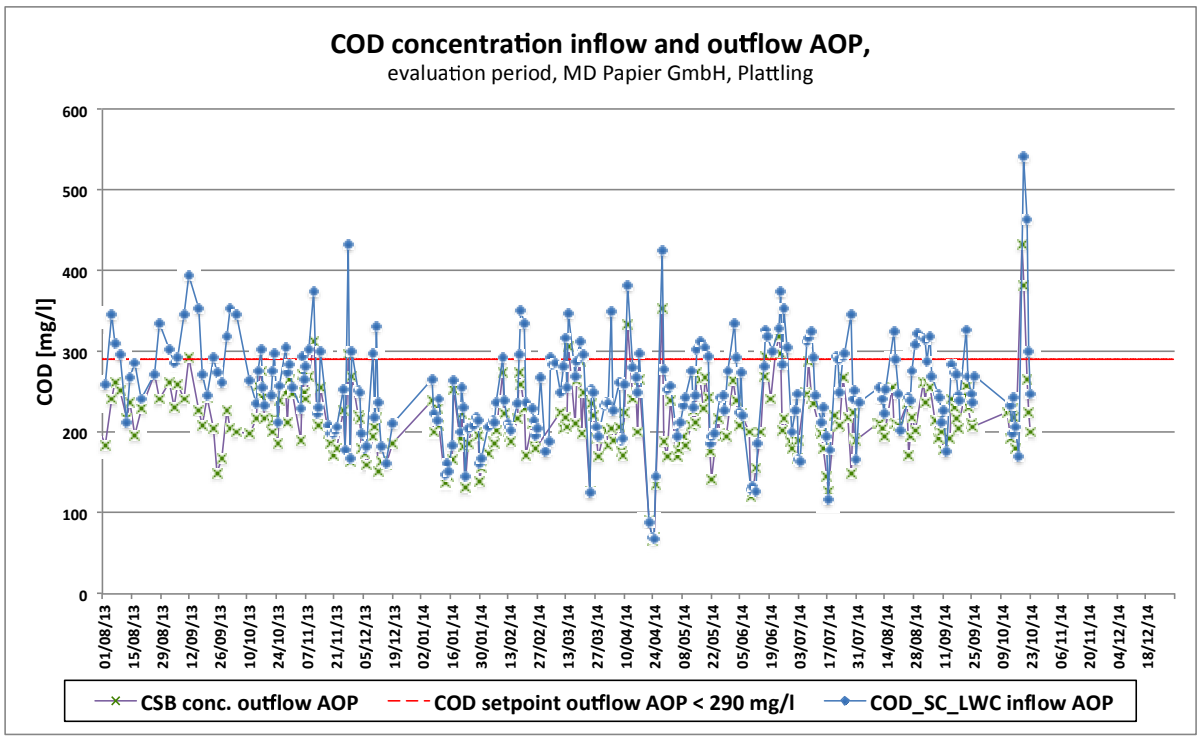

Figure 20: COD inflow and outflow concentration AOP

The 95-percentile value at the inflow AOP is in the range of 340 – 350 mg/l COD depending on whether SC or LWC effluent is treated. The 95-percentile value at the outflow AOP amounts to 289 mg/l. The required COD quality of 290 mg/l is achieved (the monitored treated effluent COD quality in the total effluent is 310 mg/l).

Figure 21 shows the BOD-concentration, **Figure 22** shows the BOD/COD-ratio inflow and outflow ozone reactor only. These figures shall demonstrate the increase of BOD at the outflow of the ozone reactor.

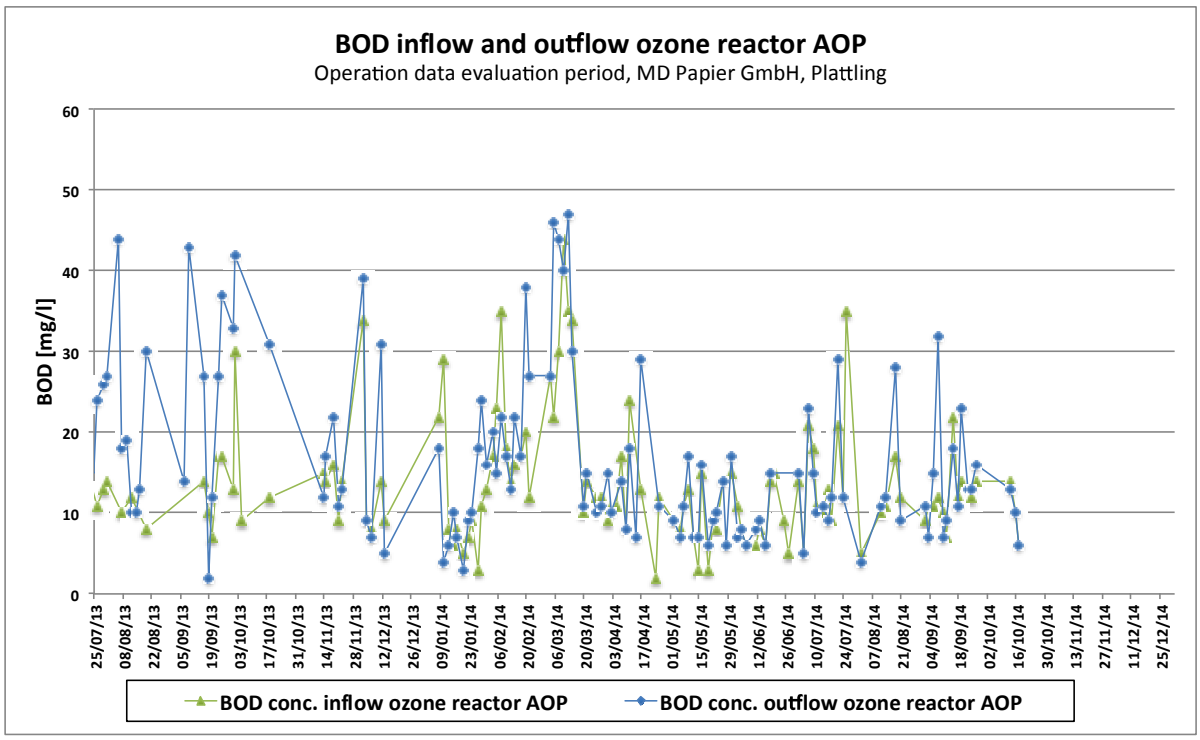

Figure 21: BOD inflow and outflow ozone reactor only

Figure 21 indicates the increase of the BOD concentration up to 30 – 40 mg/l after the ozone reactor when the ozonation is in operation. BOD concentrations at the inflow of the ozone reactor (outflow secondary clarifier) are usually expected below 15 mg/l.

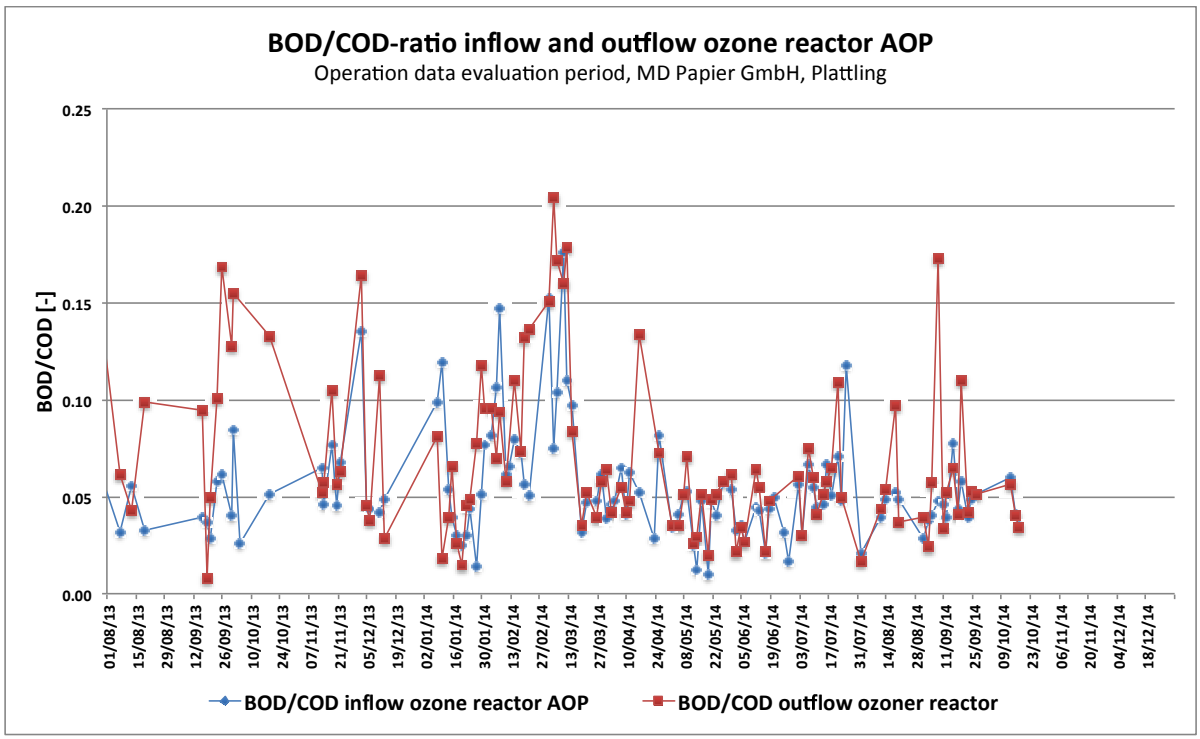

Figure 22: BOD/COD-ratio inflow and outflow ozone reactor only

Figure 22 indicates the increase of the BOD/COD-ratio up to 0.10 – 0.20 after the ozone reactor when the ozonation is in operation. BOD/COD ratios at the inflow of the ozone reactor (outflow secondary clarifier) are usually expected below 0.05.

Figure 23 shows the calculated COD concentration in the total effluent according to an average calculation considering the loads outflow WWTP LWC and SC and the total flow.

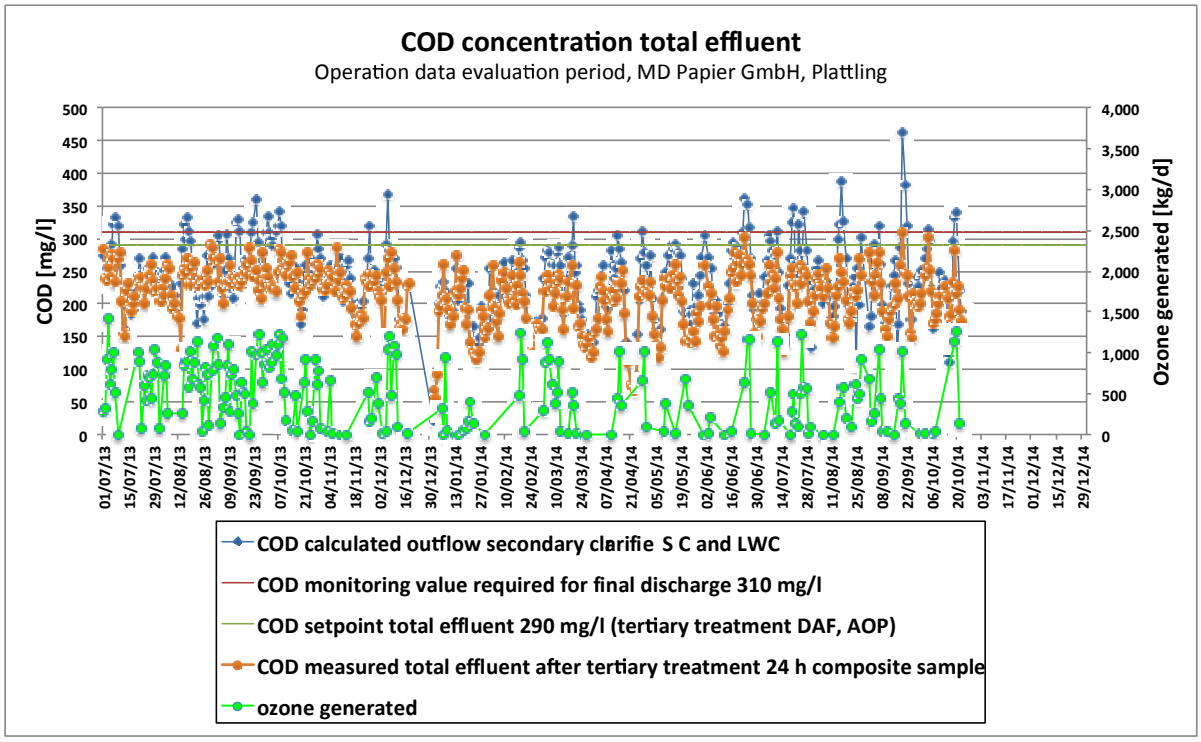

Figure 23: Calculated COD secondary clarifiers and achieved COD total effluent

Figure 23 includes the operation of the tertiary treatment stages (AOP and DAF) and is for information only of the development of the COD concentration in the final effluent. The COD concentration in the total effluent after the WWTP SC and LWC (before tertiary treatment) is calculated as an average between the loads outflow WWTP LWC and SC and the total flow. However, the COD-load eliminated is controlled mainly by operation of the AOP. DAF operation is far reduced and is operated only when required (see chapter 7.1.2).

In several cases, especially when highly bleached papers are produced, the COD exceeds the setpoint of 290 mg/l (for tertiary treatment) after the WWTP SC and LWC before tertiary treatment. The COD concentration after tertiary treatment (AOP, DAF) is kept (considerably) below the monitoring value of 310 mg/l COD. The graphical analysis also shows that AOP has been applied in several cases, although the COD

concentration would have been expected as near or already under or the COD monitoring value. This will be subject to further optimization after more operational experiences are collected (see chapter 8.1).

The COD removal efficiency in the tertiary biofilters alone without upstream ozonation is shown in **Figure 24**.

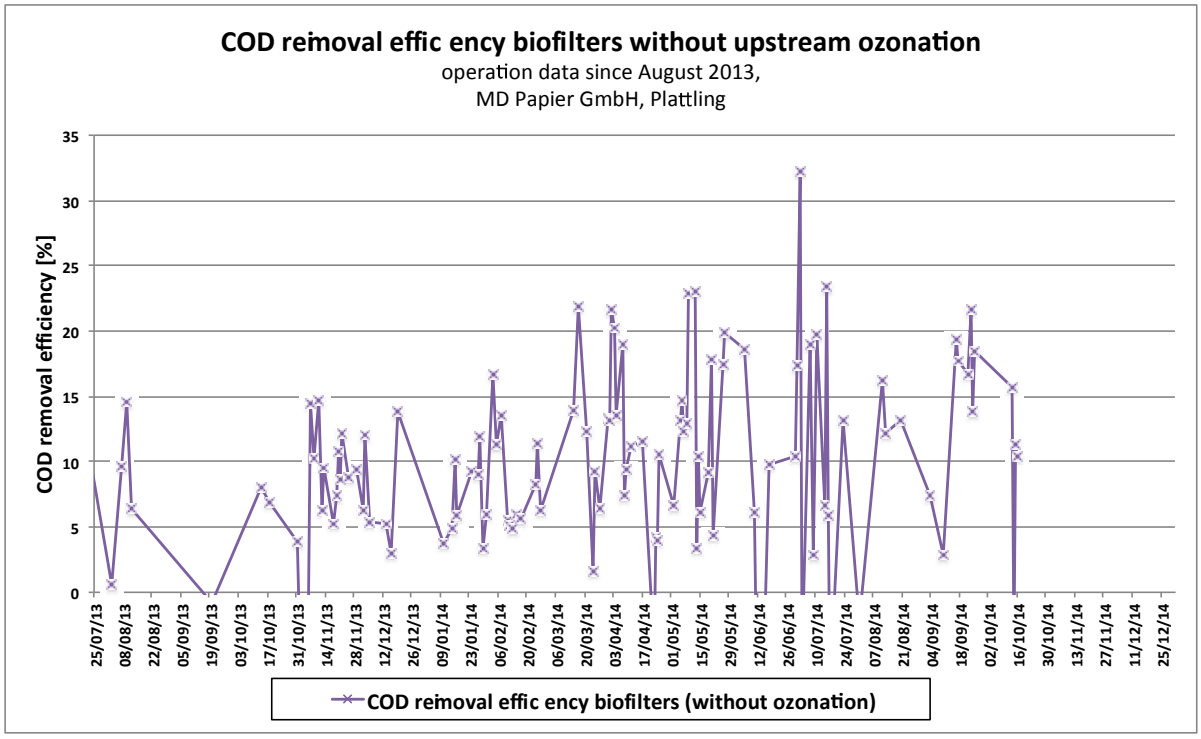

Figure 24: COD removal efficiency biofilters without upstream ozonation

The COD removal efficiency of the biofilters alone without ozonation is approx. 10 % on average as anticipated and up to approx. 22 % on the 95-percentile value (see Annex 1, Table 5). Efficiency values above 15 % are quite high and might depend on the fairly frequent shut downs of the individual paper machines and higher fluctuations in production and in the operation of the WWTP as well.

In comparison to Figure 24, the COD removal efficiency of the biofilters and the total AOP in regular operation with ozonation is shown in **Figure 25**.

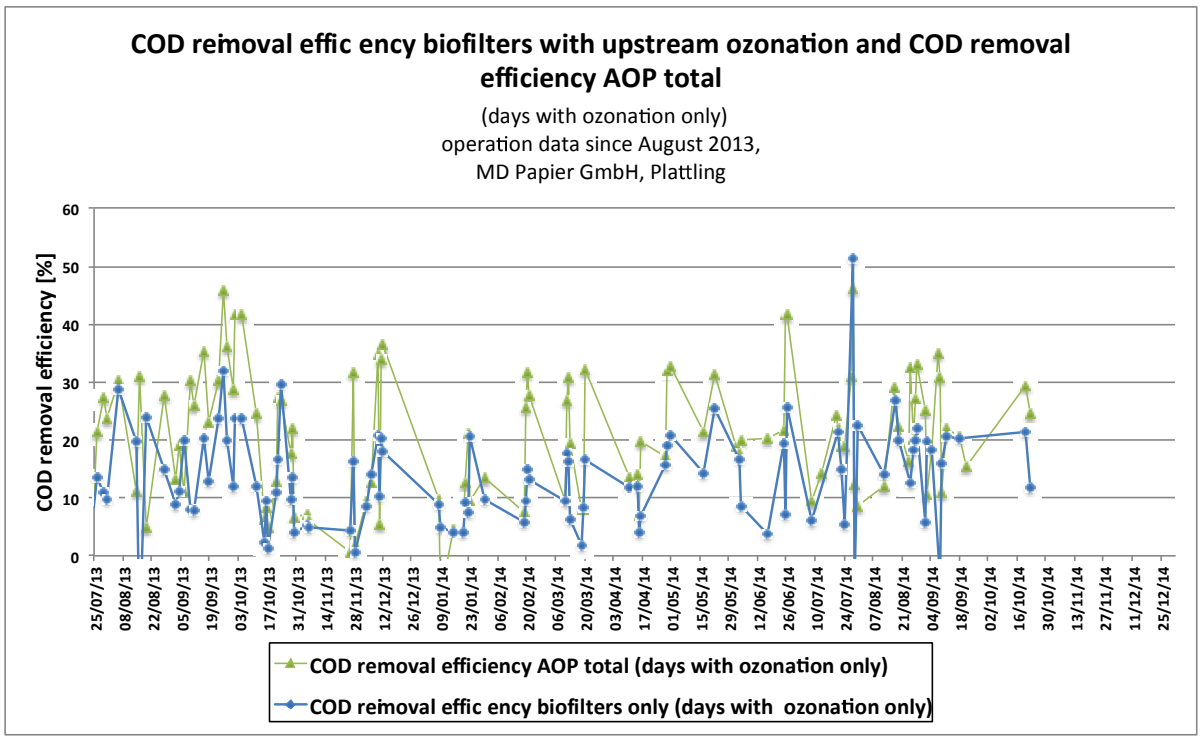

Figure 25: COD removal efficiency of the biofilters and the total AOP in normal operation (with ozonation)

The COD removal efficiency of the ozone reactors alone is approx. 8 % on average and up to approx. 22 % as 95-percentile value (see **Annex 1, Table 5**). As shown in Figure 21 and Figure 22 the BOD (and BOD/COD-ratio) increases after the ozone reactor during ozonation. The COD removal efficiency of the biofilters alone with upstream ozonation increases to approx. 14 % on average and up to approx. 26 % as 95-percentile value. The total COD removal efficiency of the AOP increases to approx. 21 % on average and up to approx. 41 % as 95-percentile value (see Annex 1, Table 5). The AOP provides the required COD removal efficiency range according to the design.

The COD load removal efficiency is shown in **Figure 26**.

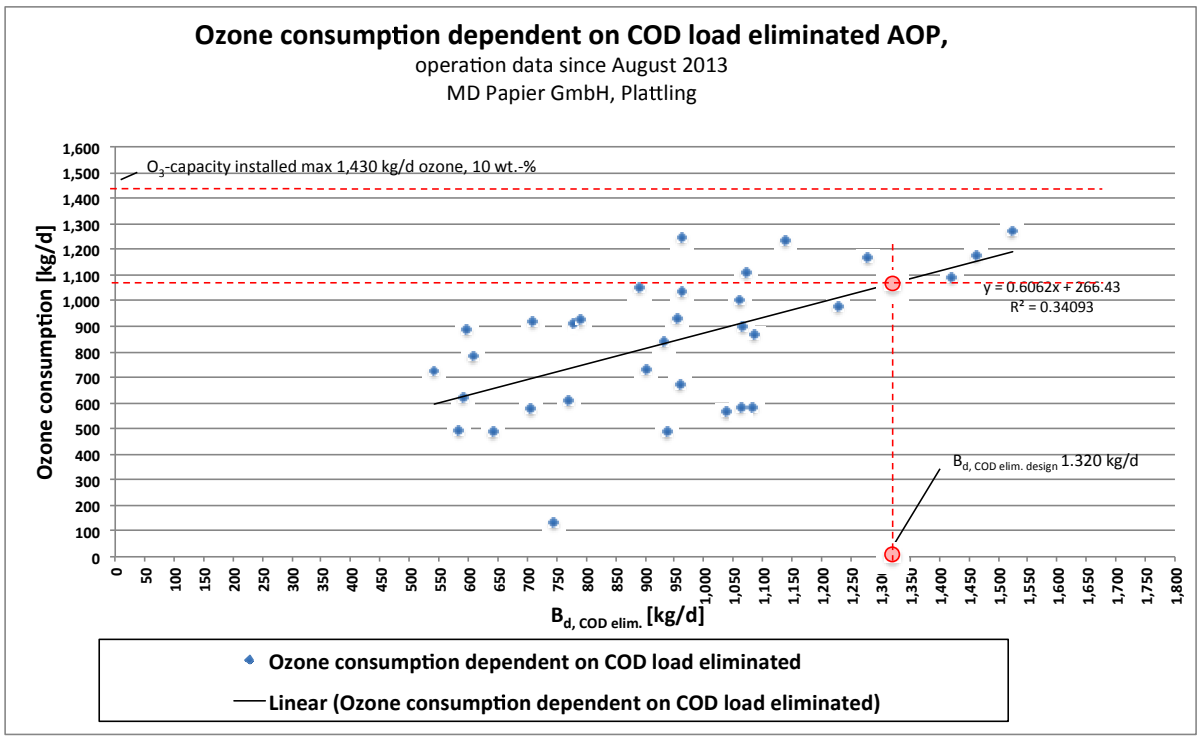

Figure 26: COD load removal efficiency AOP

The verified COD load elimination is approx. 970 kg/d on average up to 1,440 kg/d as 95-percentile (see Annex 1, Table 4 and Annex 1, Table 5). Simultaneously the ozone consumption is 870 kg/d on average up to 1,230 kg/d as 95-percentile. The installed ozone capacity is 1,430 kg/d. The AOP ensures the required COD load elimination efficiency of 1,320 kg/d and provides some additional extra capacity for higher elimination rates if required.

The specific ozone consumption depends on the eliminated COD load, which is shown in **Figure 27** and **Figure 28**.

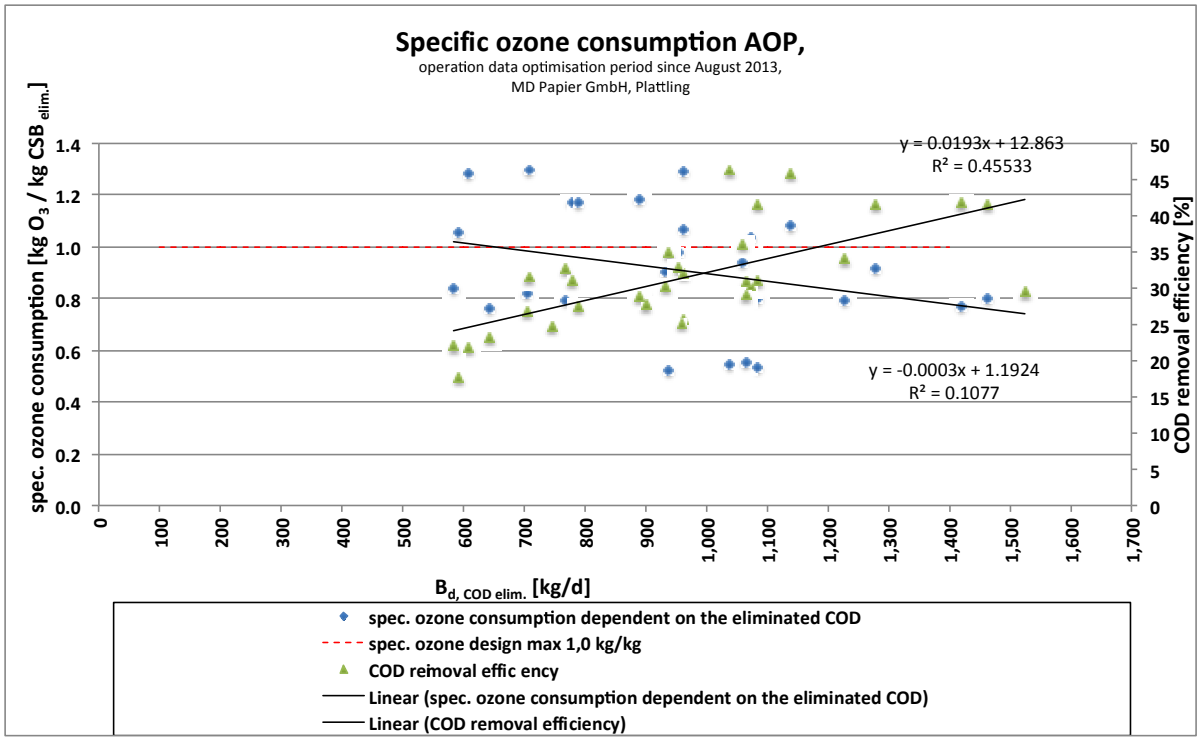

Figure 27: specific ozone consumption dependent on the eliminated COD AOP

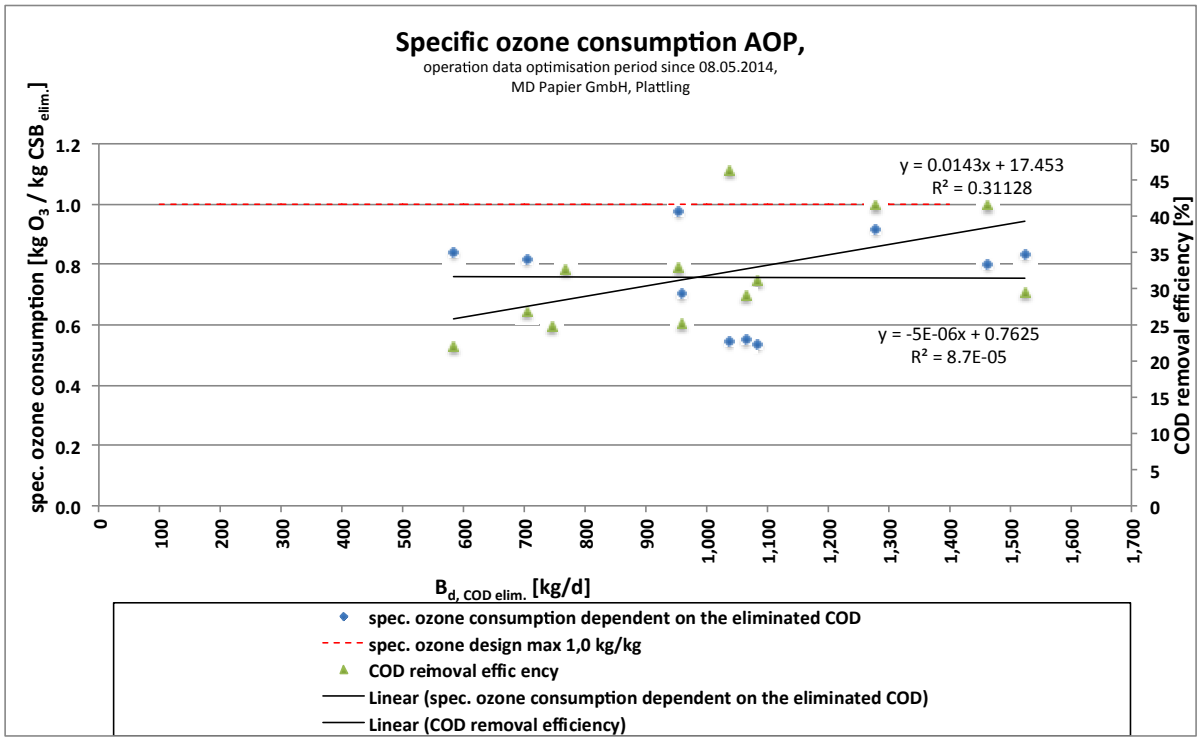

Figure 28: specific ozone consumption dependent on the eliminated COD AOP (24 h composite samples)

Figure 27 and Figure 28: the average spec. ozone consumption according to the statistical data evaluation amounts to 0.9 kg ozone per kg of COD eliminated (see Annex 1, Table 5). The average specific ozone consumption, according to the evaluated data since the beginning of May 2014 when 24 h composite samples have been taken

(Figure 28), amounts to 0.76 kg ozone per kg of COD eliminated (data calculated according to the n = 11 given data in this period). Three values are found below 0.6 kg/kg, which was the original target. However, no final determination according to the low correlation coefficient and the coefficient of determination R^2 respectively in Figure 27 and Figure 28 are valid so far. Distinctly more data is required. Additional tests need to be carried out (see also results in chapter 4.2.1 of a large scale test).

Figure 29 shows the correlation of the BOD/COD-ratio after the ozonation stage depending on specific given ozone consumption.

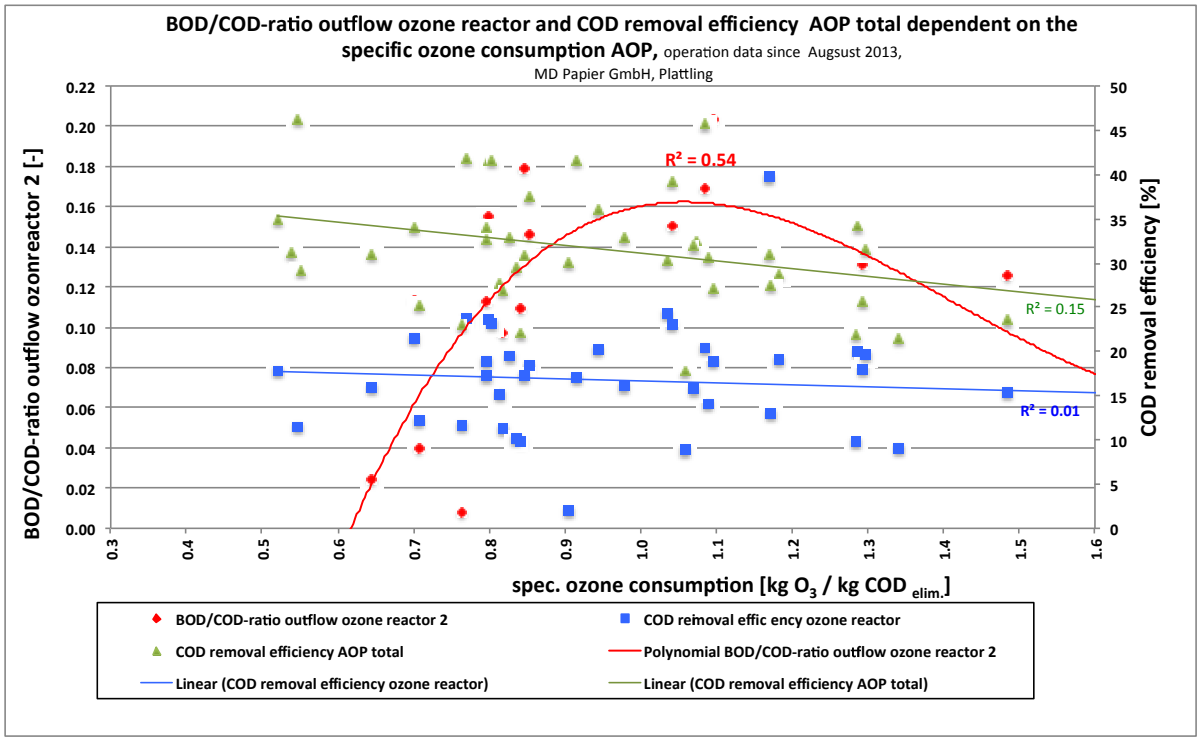

Figure 29: correlation of the BOD/COD-ratio after the ozonation stage dependent on specific ozone consumption AOP

The polynomial trendline shows a strong increase of the BOD/COD-ratio at a specific ozone consumption between 0.6 to 0.8 kg ozone per kg COD eliminated and, at the same time, an increase of the COD-removal efficiency towards lower specific ozone consumption as well. These results show that the reaction conditions for an increase in the BOD / COD ratio can in principle be created in the two-stage ozone reactor according to the theoretical approach (see chapter 2.4.3, “film-reaction). An improvement of the biodegradability and overall reduced specific ozone (and energy) consumption was one of the main objectives. However, the optimizations in the area of the two-stage ozone reactor are at the beginning. Distinctly more data are required and additional tests have to be made as already mentioned.

4.2 Results of the complementary monitoring program

4.2.1 Large scale tests

The main focus of the one-year measuring period was to collect enough operational data for statistical evaluations of treatment efficiency during times when ozonation was operated at wastewater with high COD concentrations.

The main test phase was the approach with a standard ozone distribution of 50 % into each ozone reactor.

However, longer test periods at high COD concentrations could not be expected within the one-year measuring program period. Therefore additional large-scale continuous tests were conducted in order to achieve additional examination results under more or less steady state conditions during one day.

The objective of the large-scale test was to examine the COD-removal efficiency when approx. 27 kg/h ozone corresponding to 50 mg/l ozone (a higher ozone dosage in one reactor was not possible due to restrictions in the process control system) were injected in ozone reactor one (instead of 13.5 kg/h of ozone in each reactor) and to determine the specific ozone consumption in a one stage operation.

BOD and COD were analysed within a time difference of 2 h (analyses out from grab samples). The evaluation for average values relates on the last three grab samples after 4 h of operation in order to show the results for the same water reflecting the HRT of approx. 1 h in the ozone reactor and the biofilters.

The large scale-test results with an ozone diffusion in reactor one with a capacity of 27 kg/h are shown in **Figure 30** to **Figure 33**.

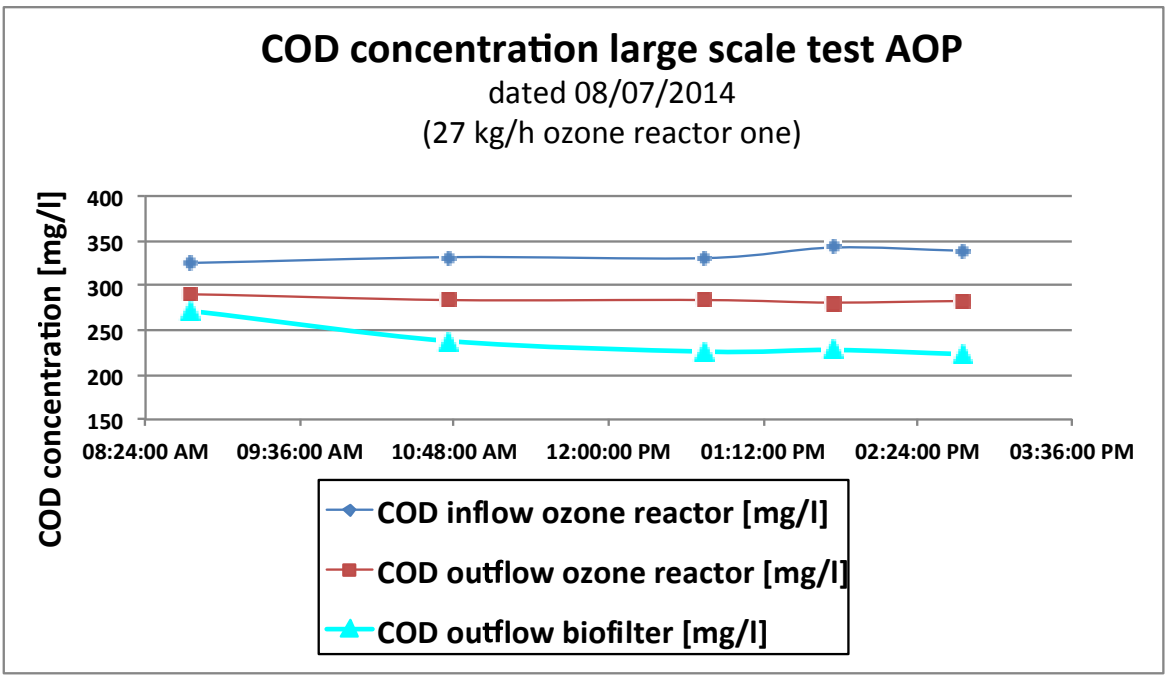

Figure 30: Reduction of the COD concentration inflow ozone reactor one and outflow biofilter (ozone reactor one capacity 27 kg/h ozone)

The line of the ozone concentration shows a more or less constant COD reduction from the early beginning of approx. 340 mg/l COD inflow to approx. 280 mg/l outflow ozone reactor (COD elimination is approx. 60 mg/l in the ozone stage). The line of the COD concentration in the outflow of the biofiltration shows a decrease from approx. 280 mg/l inflow biofiltration versus outflow biofiltration (outflow AOP) to 225 mg/l (COD elimination is approx. 55 mg/l in the ozone stage). The total COD elimination amounts to approx. 115 mg/l.

The biodegration in the biofiltration after ozonation starts immediately. Approx. 100 mg/l of COD are eliminated after about two hours operation time. The nearly full COD elimination is reached after approx. 3 – 4 h ozonation.

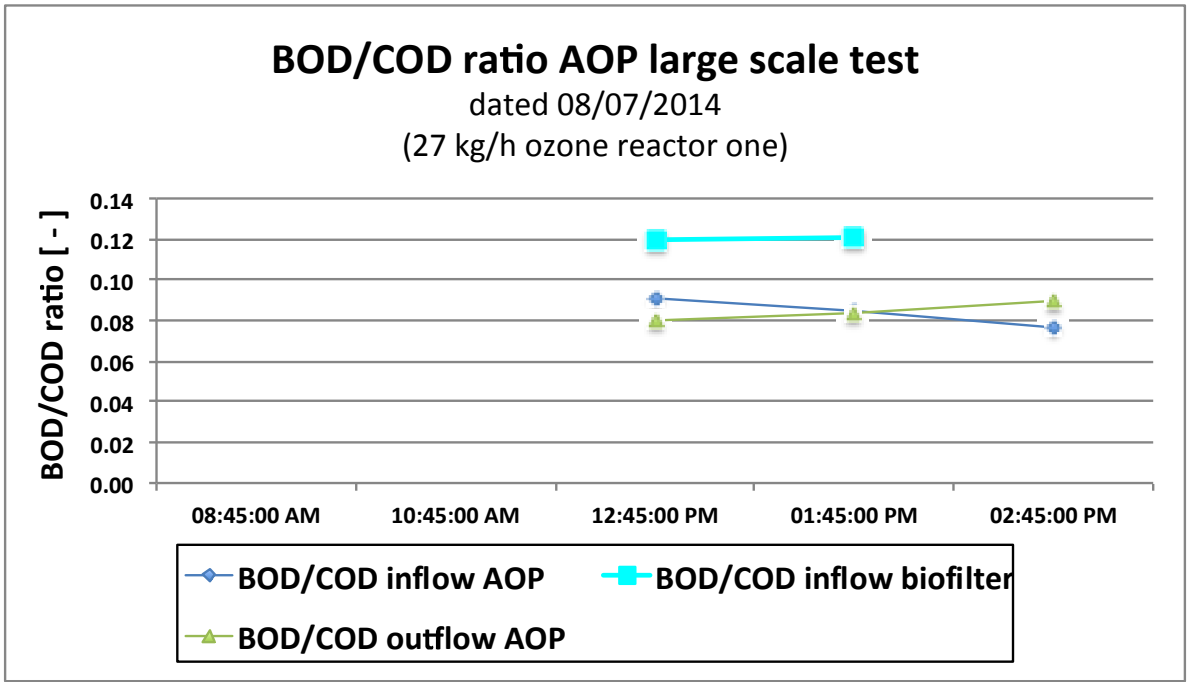

Figure 31: Increase of the BOD/COD-ratio inflow ozone reactor one and outflow bio-filter (ozone reactor one capacity 27 kg/h ozone)

The grab samples were taken and analyzed after approx. 4 h of operation (the first two sampling points are missing for this reason here). The BOD/COD-ratio increases from 0.08 at the inflow ozone reactor to 0.12 at the outflow of the ozone reactor. After biofiltration the BOD/COD-ratio decreases again down to the original level.

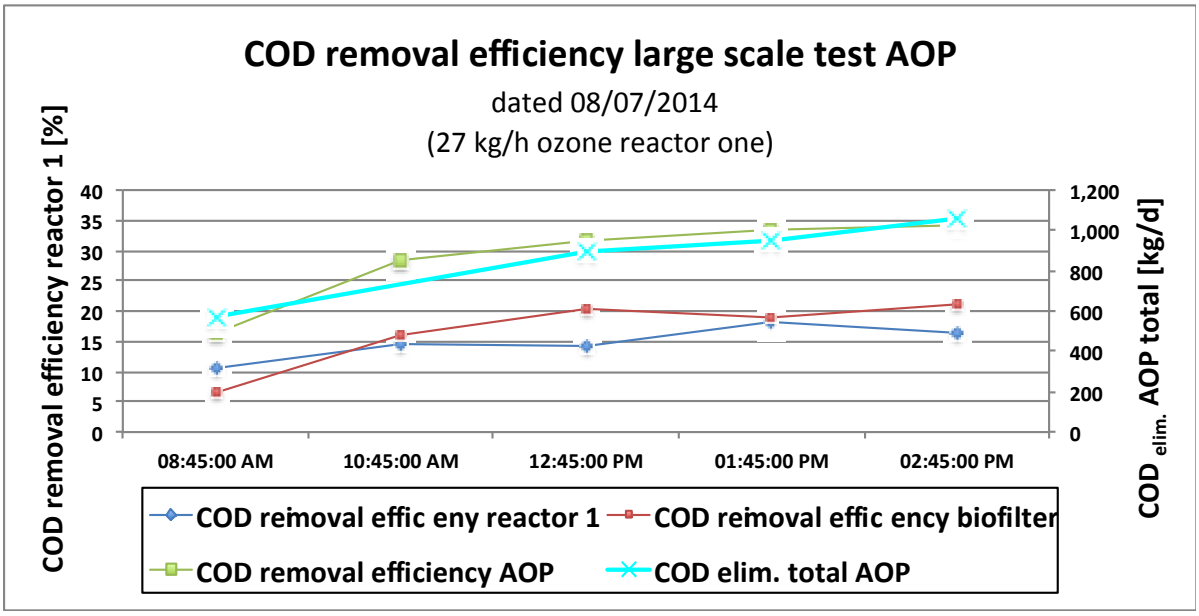

Figure 32: COD elimination and efficiency inflow ozone reactor and outflow biofilter (ozone reactor one capacity 27 kg/h ozone)

The total COD removal efficiency is after 4 h already above 30 % and increases after 5 h further to approx. 35 %. The COD-removal efficiency in the ozone reactor amounts

to approx. 15 % and of the biofiltration to approx. 20 %. The up-scaled eliminated COD load in this test amounts to approx. 1,060 kg/d

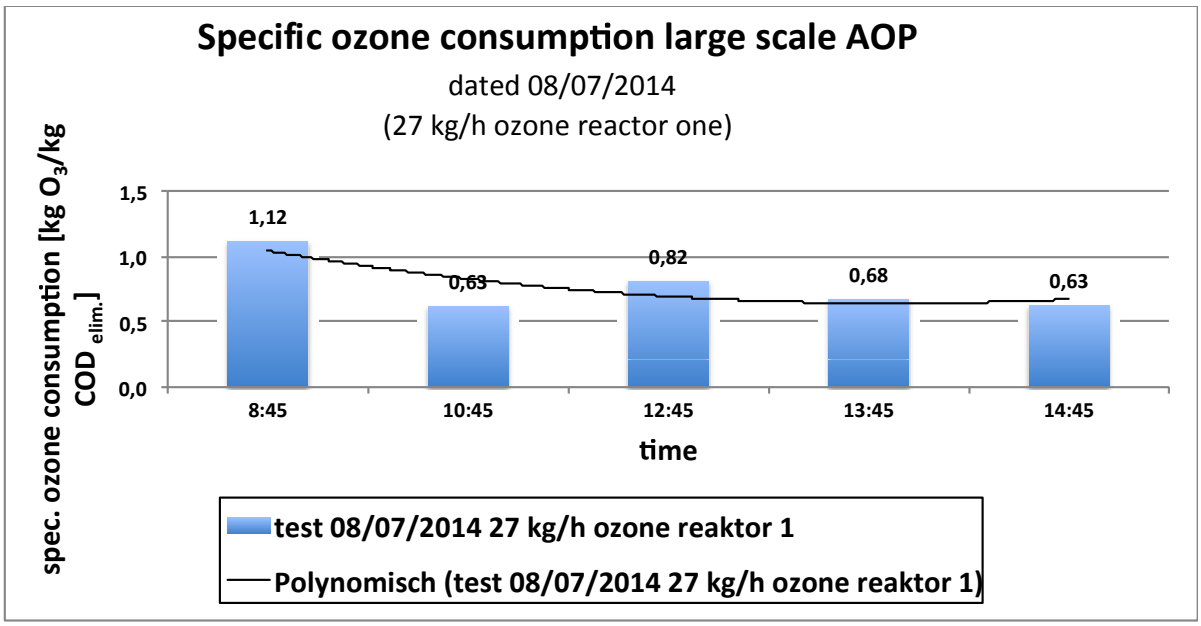

Figure 33: COD-removal efficiency at a high ozone input in reactor one AOP (ozone reactor one capacity 27 kg/h ozone)

The specific ozone consumption amounts to 0.63 kg ozone per kg COD eliminated which is below the statistical evaluated value of 0.8 - 0.9 kg/kg in normal operation (see Figure 27 and Figure 28). More tests are required for verification of the results. However, the results indicate a further optimization potential. It is planned to test different ozone distribution set points as well as the examination of one and two stage operation tests immediately after one another

The qualitative color degradation and a further decrease of turbidity in the outflow AOP (outflow biofiltration) is shown in **Figure 34**.

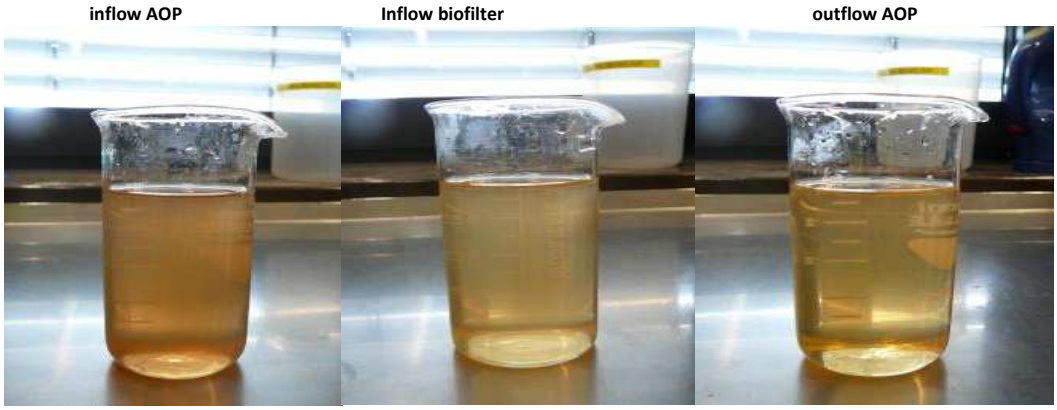

Figure 34: Removal of color and turbidity AOP, photos during the large scale test

4.2.2 Evaluation and results of large scale the batch test and analyses

The effect of ozone in wastewater applications is often studied in batch tests, provided that continuously operated ozone tests cannot be performed in pilot tests. However, the disadvantage of batch tests lies in the fact that ozone is more and more consumed due to the accumulation of by-products.

In preparation of the complementary tests and analyses as described in the following chapter the effect of a far reaching ozonation in a large scale batch test was studied additionally.

In normal operations, there is a continuous flow through reactor 1 and 2. The retention time is 30 min. It is only possible to take samples from effluent reactor 1 and reactor 2. To measure the progress of the transforming or elimination of substances depending on the time and increasing ozone input is not possible. Therefore a batch test has been carried out in ozone reactor 1. Without continuous flow it was possible to take samples continuously to follow the progress of the chemical reaction. For this test, the connection to reactor 2 was closed to avoid unintended mixing with the 2nd reactor. The internal circulation has to be modified to guarantee an optimal mixing inside the reactor (**Figure 35**).

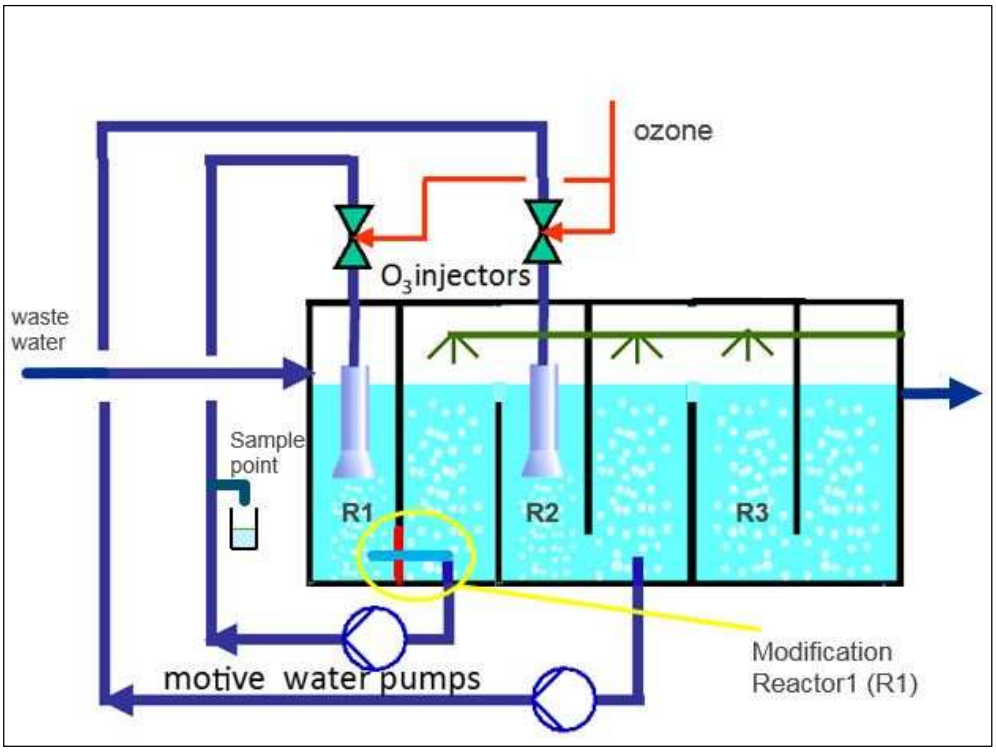

Figure 35: modification of reactor 1 for batch test

The transformation of COD into BOD is shown in **Figure 36**.

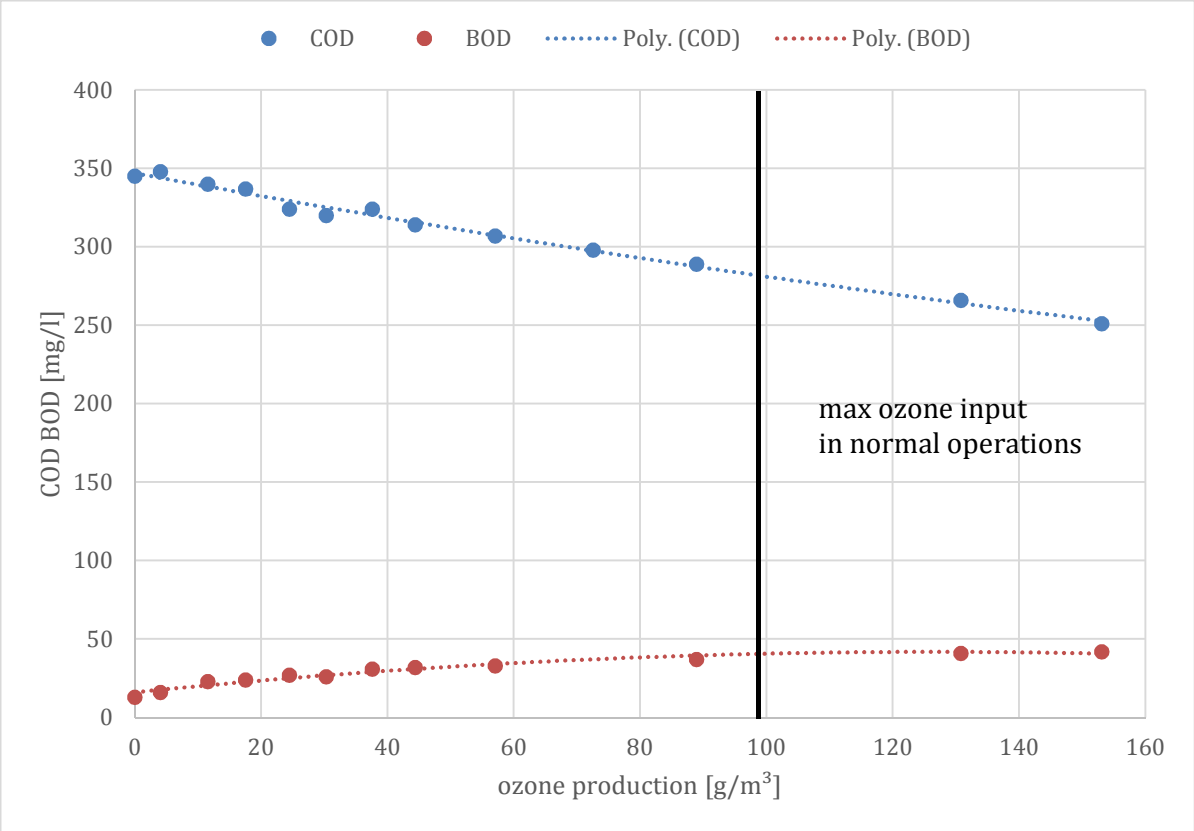

Figure 36: Oxidation of COD and generating BOD in batch test

Approximately 98 g ozone per liter wastewater matches with 30 min retention time. This is the maximum ozone input under normal operation conditions. About 40 mg/l BOD could be created from COD after an input of 98 g O_3 per liter. The BOD increases close to 50 mg mg/l within this ozonation level and does not further increase. However, an additional 60 mg/l COD have been fully oxidized and completely removed from wastewater.

The ability of ozone to oxidize the persistent COD from papermill wastewater is well proved with this batch trial and the results from continuous operations. Nevertheless, the target in continuous 2-stage operations is to minimize the fully oxidation of COD and maximize only the transformation from non-biodegradable COD to BOD (**Figure 37**). In batch test this effect of fully oxidation is much higher (as already mentioned above).

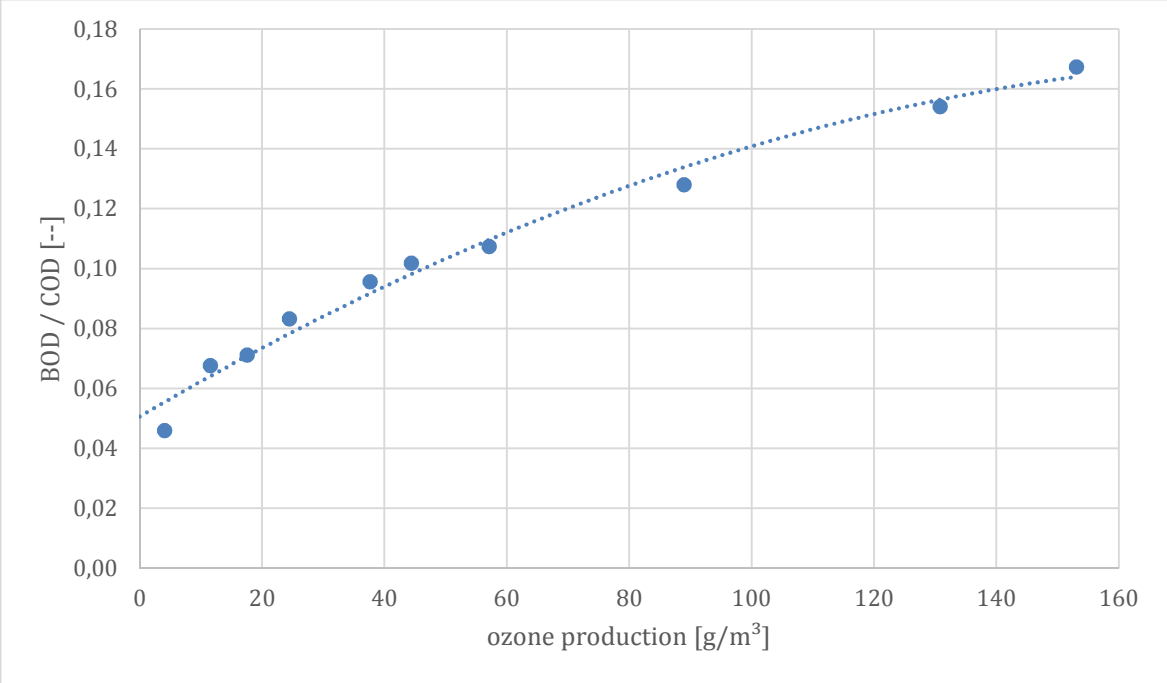

Figure 37: BOD / COD ratio versus ozone produced in batch trial

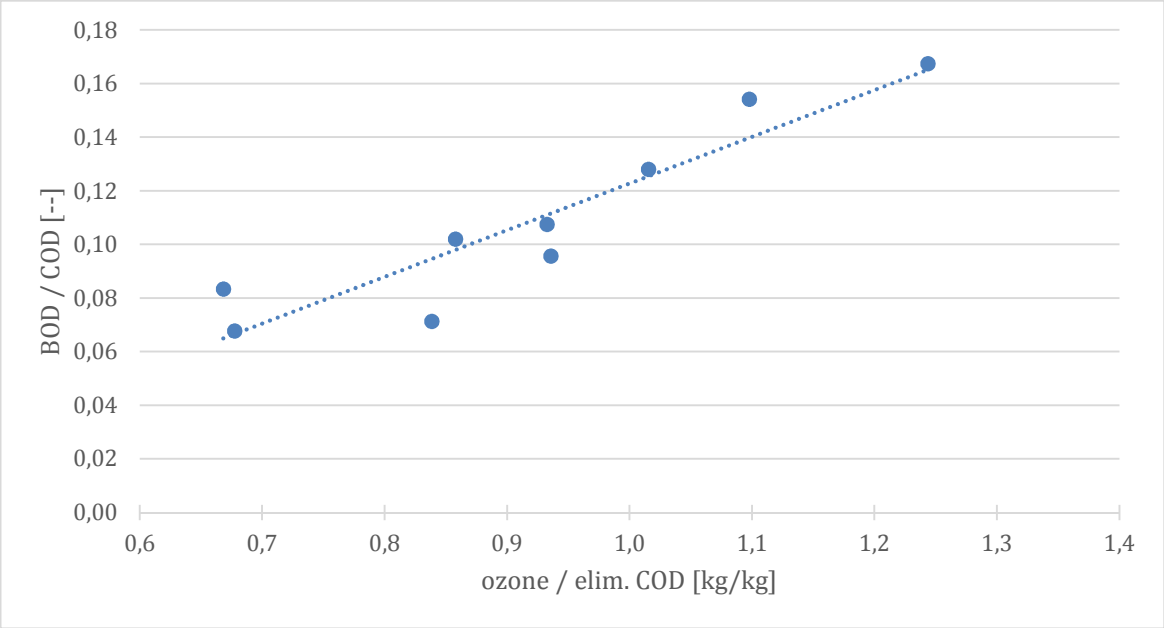

Figure 38: BOD / COD ratio versus specific ozone consumption in batch trial

The BOD/COD ratio was increased during the entire batch trial. In continuous operations a maximum in BOD/COD ratio with increasing specific ozone input could be observed. However, the specific ozone consumption increases above values of 1.0 kg ozone per kg COD eliminated which means that organic by-products are more and more oxidized (which is not the target as well). The conditions in batch trials are therefore different to continuous flow reactors because the optimum of the BOD/COD-ratio cannot be exactly determined without

continuously biodegradation at an optimized (reduced) specific ozone consumption including the biochemical oxidation effect in the biofiltration. Important for further optimization are only the results from continuous ozonation tests as explained above in chapter 4.2.1

The main focus of the complementary tests and analyses was the elimination of micro pollutants, chelating agents, AOX and with a special focus as well as on endocrine disruptors.

Moreover, meaningful results in a large-scale test and a relatively large volume compared with laboratory or pilot plant scale are to be expected.

The results are explained in the following chapters below.

4.2.3 Evaluation and results of the complementary tests and analyses

4.2.3.1 Measurement of organic pollutants removal

Some special organic pollutants (complexing agents, AOX, Bisphenol A, polycyclic aromatic hydrocarbons, endocrine disrupting substances, phthalates and perflourinated compounds) have been measured in normal operation mode with continuous flow.

However, it was expected that the wastewater concentration of the groups of substances as mentioned above are very low or are even below detection limits at MD Papier GmbH in Plattling. In this case it was agreed upon to add the relevant substances to a detectable concentration in the wastewater if required.

Therefore tests with organic pollutants have also been performed in batch mode. During the batch test with original LWC wastewater, the content of complexing agents, AOX and Bisphenol A has been increased with chemicals to reach a higher influent concentration level compared with usual levels. This has been achieved by applying the original mill complexing agent (DTPA/EDTA), Tetrachloromethane for AOX and Bisphenol A from the laboratory. Also the elimination of coloring substances could be observed.

4.2.3.2 Chelating agents DTPA and EDTA removal

DTPA (diethylenetriaminopentaacetic acid) and EDTA (ethylenediaminetetraacetic acid) are chelating agents, which are important for reducing the concentration of heavy metals, which might react with the peroxide during peroxide bleaching of the mechanical or chemical pulp. They are not easily biodegradable in wastewater, but there is a certain amount of elimination by retention in pulp and adsorption in the sludge. The DTPA / EDTA concentration was measured during normal AOP operations with LWC and SC wastewater. Also at the batch test with LWC wastewater.

UPM Plattling is using two different products. Product 1 is a mixture of 40% EDTA / 60% DTPA. The concentration of active ingredient in the commercial chelating agent bulk is 25%. Product 1 is mainly used at SC mill. Product 2 is 100% DTPA with a concentration of 35 – 40% and is mainly used at LWC mill. The typical concentration of mechanical pulp peroxide bleaching is 0,5 – 0,6 wt.-% (chelating agent commercial bulk / bone-dry mechanical pulp).

The elimination of non-readily biodegradable chelating agents in normal operations for several days is shown in Table 8.

Table 8**:** Elimination of complexing agents in normal operations over several days

Sample #	Para-meter	Mill	Influent Ozon Reactor	Effluent Ozone Reactor	Elimination Ozone Reactor	Effluent Biofilter	Elimination Biofilter	Elimination total
			mg/l	mg/l	%	mg/l	%	%
1	DTPA	LWC	5,20	3,43	34%	2,24	35%	57%
2	DTPA	LWC	3,05	0,33	89%	0,27	19%	91%
3	DTPA	LWC	3,90	0,60	85%	0,60	0%	85%
4	DTPA	SC	2,69	0,52	81%	0,39	25%	86%
5	DTPA	SC	4,50	1,40	69%	1,20	14%	73%
1	EDTA	LWC	1,60	1,05	34%	0,85	19%	47%
2	EDTA	LWC	0,34	0,16	53%	0,16	3%	54%
3	EDTA	LWC	6,70	0,80	88%	0,60	25%	91%
4	EDTA	SC	3,42	0,90	74%	0,74	18%	78%
5	EDTA	SC	9,40	3,70	61%	3,50	5%	63%
Average	**DTPA**				**71%**		**19%**	**78%**
Average	**EDTA**				**62%**		**14%**	**67%**

AOP was running in normal operation mode with both reactors and maximum ozone production on days when additional COD removal capacity was necessary to keep the COD limit. The elimination of DTPA is higher than EDTA. The elimination is mainly achieved by oxidation in ozone reactors and a smaller share in biofilter, probably due mainly to adsorption.

The elimination of DTPA and EDTA is shown in **Figure 39**.

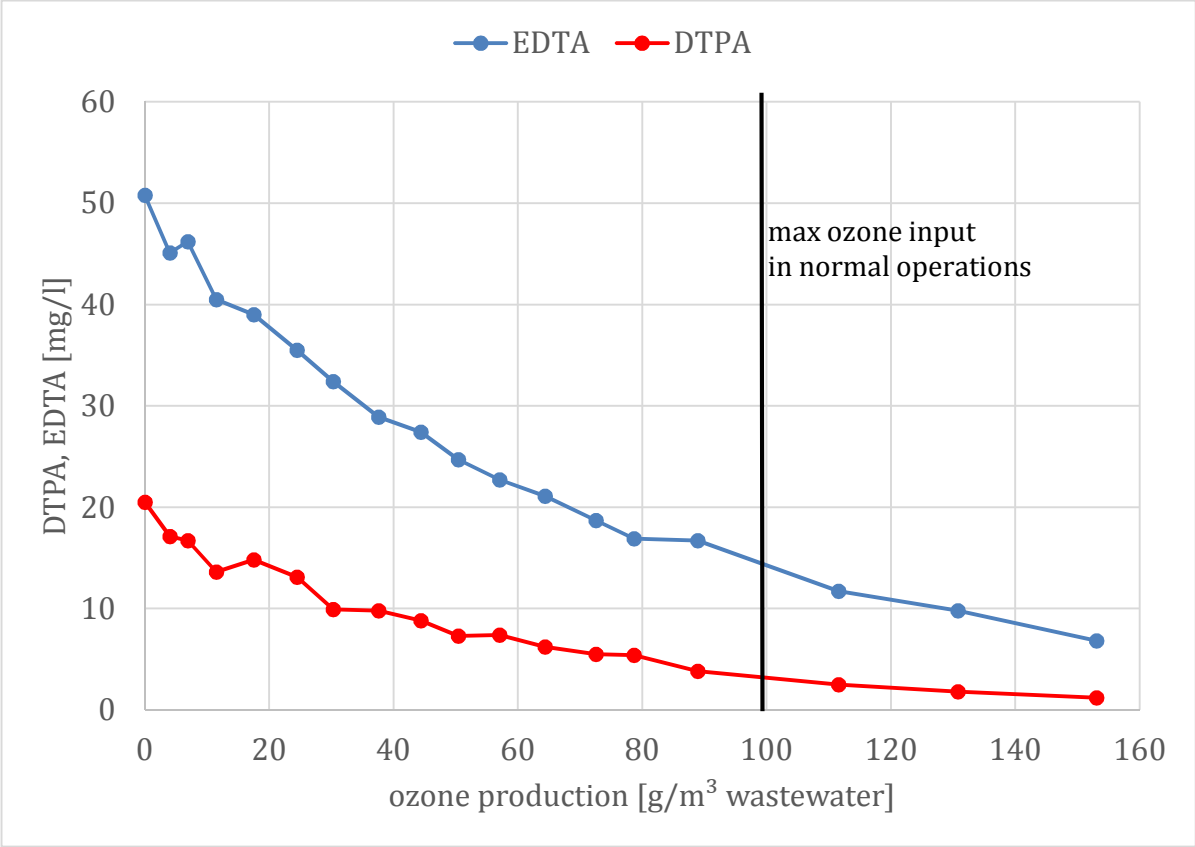

Figure 39: Elimination of complexing agents in batch test

The elimination with ozone oxidation starts with high efficiency. By decreasing the concentration of DTPA/EDTA, the elimination ratio is reduced. According to normal operations (510 m³/h wastewater, 50 kg/h ozone), which is equal to 30 min and ~ 98 g/m³ ozone input in batch trial, the elimination of DTPA / EDTA is 85% / 70%. With half ozone production, the elimination is already 65% / 50%.

4.2.3.3 AOX removal

One of the main sources of AOX (adsorbable organic halogens) in the paper industry is the epichlorohydrin resin recovered from wet strength paper from the deinking plant. A very small amount is also coming from organic halogen-contained biocides. The wastewater related permit limit for AOX for Plattling mill is very low (0,64 mg/l). There is no emission value associated with BAT for this kind of paper production. Only two limit breaches occurred during the last 3 years (0,79 and 0,74 mg/l).

The elimination of AOX in normal operations is shown in **Table 9**.

Table 9**:** elimination of AOX in normal operations

Sample #	Para-meter	Mill	Influent Ozone Reactor	Effluent Ozone Re-actor	Elimina-tion Ozone Re-actor	Effluent Biofilter	Elimina-tion Biofil-ter	Elimina-tion total
			mg/l	mg/l	%	mg/l	%	%
1	AOX	LWC	0,42	0,14	67%	0,22	increase	48%
2	AOX	LWC	0,85	0,16	81%	0,11	31%	87%
3	AOX	SC	1,30	0,13	90%	0,09	31%	93%
Average	**AOX**				**79%**		**31%**	**76%**

Ozone can be used to eliminate AOX very efficiently. The elimination in the biofilter is very low, performed mainly by adsorption. There is a small increase in the first sample between the effluent ozone reactor and effluent biofilter. This could be due to desorption from biofilm or variation in AOX analysis.

The continuous monitoring of AOX in the effluent to the river Isar (common effluent WWTP LWC and SC), required by wastewater permit, shows that the AOX could be decreased by an average of 35 %, when the AOP is in operation. This result is based on nearly 70 measurements (Table 10).

Table 10**:** AOX monitoring in WWTP effluent

	Without AOP	With AOP	reduction
number of samples	52	19	
max	0,79 mg/l	0,49 mg/l	
average	0,20 mg/l	0,13 mg/l	35%

AOX elimination was also monitored in the batch test. The concentration has been increased with an organic chlorine compound to reach a higher wastewater concentration.

Due to the harmful properties of epichlorohydrin another substance has been chosen for this test. Tetrachloromethane was available from the mill laboratory. This is not a typical substance in the paper industry, but a very good AOX source. It is also harmful but easier to handle.

The test was done with LWC wastewater.

The AOX elimination in batch tests is shown in **Table 11** and **Figure 40**.

Table 11**:** Elimination of AOX in batch test

sample #	reten-tion time [min]	ozone pro-duction / wastewater [g/m³]	AOX Lab 1 [mg/l]	AOX Lab 2 [mg/l]	AOX Lab 3 [mg/l]	AOX Lab 1 elimination ref. sample 1	AOX Lab 2 elimination ref. sample 1	AOX Lab 3 elimination ref. sample 1
1	0	0	1,6	0,26	0,45			
2	4	4			0,41			9%
3	6	7	1,4			13%		
4	9	12	1,4	0,25	0,20	13%	5%	56%
5	13	18	1,3	0,21	0,12	19%	20%	73%
6	19	24	1,3		0,07	19%		84%
7	23	30	1,1	0,20	0,35	31%	23%	22%
8	29	38			**0,20**			56%
9	34	44	0,63	0,17	0,12	61%	36%	73%
10	39	50			0,19			58%
11	44	57	0,47	0,16	**0,16**	71%	37%	64%
12	48	64			0,14			69%
13	54	73	0,42	0,17	0,28	74%	34%	38%
14	58	79			0,20			56%
15	65	89	0,34	0,15	0,11	**79%**	**41%**	**76%**
16	79	112	0,29		0,07	**82%**		**85%**
17	94	131	0,22	0,12	0,18	86%	56%	60%
18	110	153			0,12			

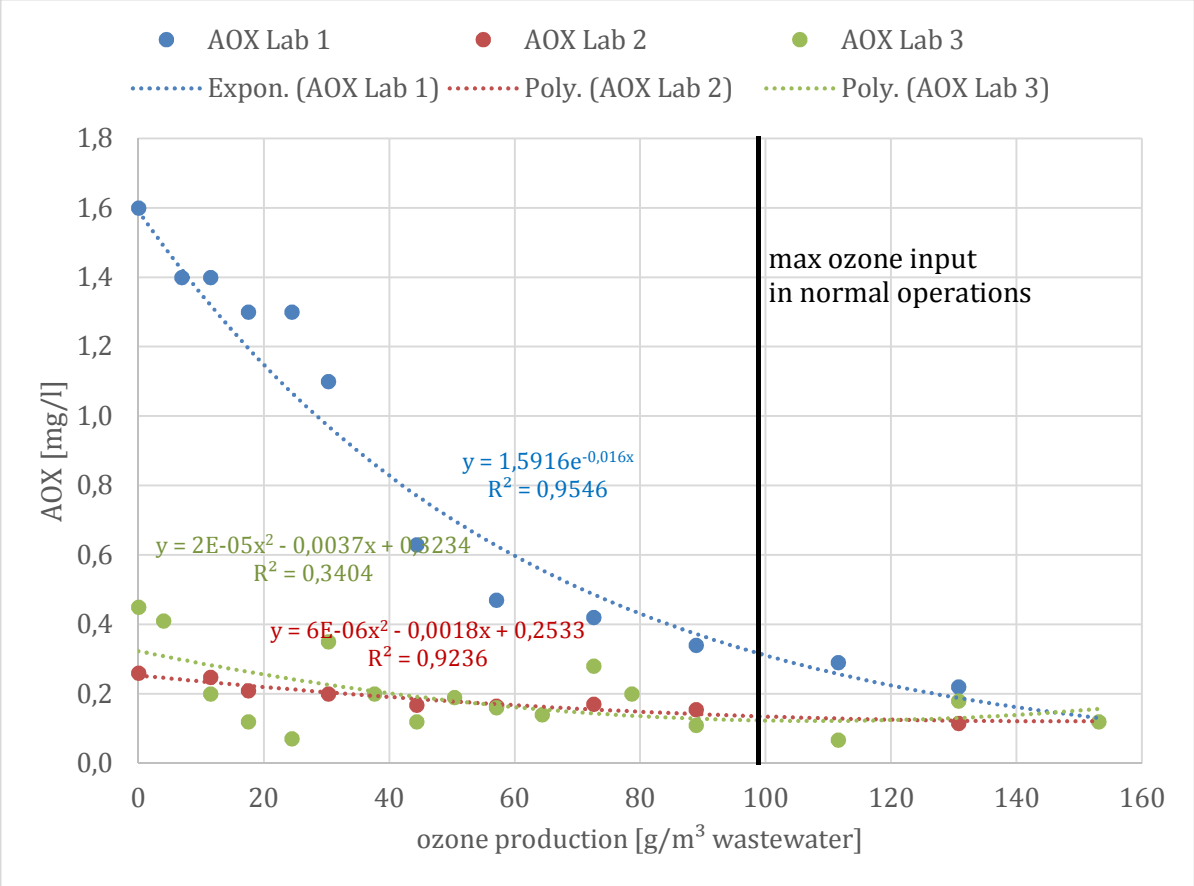

Figure 40: Elimination of AOX in batch trial

All samples have been analysed by 3 different laboratories. The results of 2 laboratories are on the same level. The third lab (Lab 1) starts with a much higher concentration. The parameter AOX shows very often this variation of analyses. One explanation could be, that it depends on the different sample preparation and operation methods of the external laboratories, which are not exactly known in this case. The efficiency of AOX elimination during normal operation (98 g/m³ ozone, 510 m³/h wastewater, 50 kg/h ozone) is about 80%.

4.2.3.4 Bisphenol A (BPA) removal

BPA has been widely used since the 1950s and is used in thermal paper for cash register receipts and as an additive in plastic products. Therefore it can be found in recovered paper raw material from the deinking plant.

Typical BPA contents are listed in Table 12 (Source: Abschlussbericht zur wissenschaftlichen Studie “Ausmaß der Migration unerwünschter Stoffe aus Verpackungsmaterialien aus Altpapier in Lebensmitteln“ Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz, 31.05.2012).

Table 12**:** Typical BPA contents in waste paper

waste paper	**unit**	**BPA (min – max)**
newspaper	mg/kg paper	1, 6 – 6,5
magazines	mg/kg paper	< LOD – 7,6
flyer, advertising brochure	mg/kg paper	< LOD – 3,9
office waste paper	mg/kg paper	< LOD – 111
special paper	mg/kg paper	< LOD – 12,5
board	mg/kg paper	8,6 – 18,8
glued products	mg/kg paper	< LOD – 17,0

The typical content of waste paper at Plattling deinking plant is a mix from magazines, flyers, advertising brochures, office waste paper and special paper (wet strength labels).

BPA exhibits hormone-like properties (endocrine disruptors). The elimination in the WWTP and AOP in normal operations is shown in Table 13.

Table 13**:** Elimination of BPA in normal operations

Sample #	Parameter	Mill	Influent biological stage	Influent Ozone Re-actor	Effluent Ozone Re-actor	Effluent Biofilter
			µg/l	µg/l	µg/l	µg/l
1	Bisphenol A	LWC	0,11	< 0,05	< 0,05	< 0,05
2	Bisphenol A	SC	< 0,10	< 0,05	< 0,05	< 0,05

The concentration of BPA in the influent to the biological stage of WWTP is very low. The concentration after MBBR (Moving Bed Biofilm Reactor) and aerated sludge basin was below detection limit (0,05 µg/l).

A second measurement in batch test with increased BPA was carried out. The very low BPA content in the original wastewater has been increased by adding BPA.

The results in batch test AOP reactor 1 are shown in Table 14.

Table 14**:** Elimination of BPA in batch test ozone reactor 1

retention time	O_3 input	O_3 input concen-tration	Bisphenol A
min	kg	g/m³ water	µg/l
0,0	0,0	0,0	0,09
5,0	0,3	4,0	0,09
10,2	0,9	11,5	0,07
20,2	2,0	24,5	0,08
30,3	**3,0**	37,6	0,06
45,1	**4,6**	57,1	< 0,04
59,6	6,4	78,7	< 0,04

The elimination of BPA is shown in **Figure 41**.

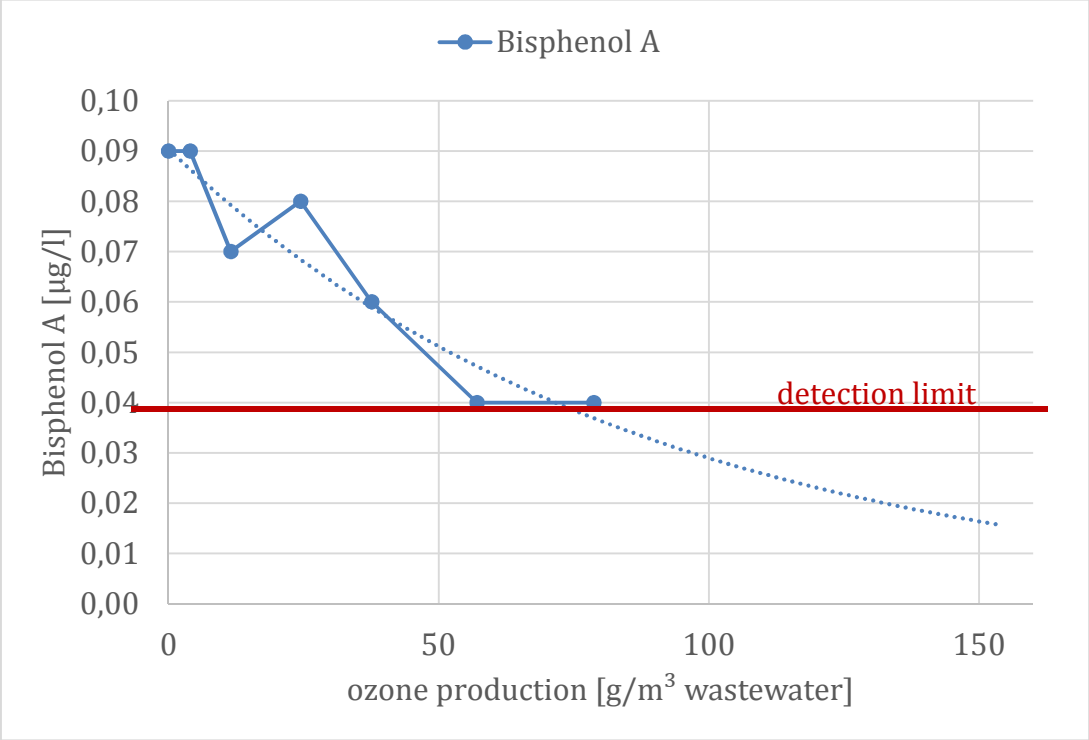

Figure 41: Elimination of BPA in batch test ozone reactor 1

4.2.3.5 Polycyclic Aromatic Hydrocarbons (PHA) removal

In contrast to the MOAH (mineral oil aromatic hydrocarbons) are the PHA mainly not or little alkylated aromatic substances. Here, the 16 PHA according to US Environmental Agency Protection were analyzed (so-called "EPA-PHA") for the significant environmental PHA. Newspapers (average PAH content 2,6 mg / kg paper) and also magazines (average 0.8 mg

/ kg paper) could be identified as the main source of contamination of EPA-PHA in the recycling process. This is probably due to the use of the black pigment "Carbon Black" in offset inks for newspapers and also magazines. This black pigment is obtained from industrial grimes, which are optimized in respect to PHA levels, but it is still containing.

EPA-PHA have been identified as carcinogenic and mutagenic and are listed as “Priority Pollutants”.

Typical PHA (16 PHA, defined by US Environmental Protection Agency EPA) contents are listed in Table 15 (Source: Abschlussbericht zur wissenschaftlichen Studie “Ausmaß der Migration unerwünschter Stoffe aus Verpackungsmaterialien aus Altpapier in Lebensmitteln“ Bundesministerium für Ernährung, Landwirtschaft und Verbraucherschutz, 31.05.2012).

Table 15**:** Typical PHA contents in waste paper

waste paper	**unit**	**PHA (min – max)**
newspaper	mg/kg Papier	1, 4 – 4,0
magazines	mg/kg Papier	0,1 – 1,3
flyer, advertising brochure	mg/kg Papier	< 0,1 – 1,0
office waste paper	mg/kg Papier	< 0,1 – 0,7
special paper	mg/kg Papier	< LOD – 12,5
board	mg/kg Papier	8,6 – 18,8
glued products	mg/kg Papier	< LOD – 17,0

PHA can be found in wastewater from deinking plants and in deinked pulp. A screening was done in both wastewaters LWC and SC (Table 16).

Table 16: Polycyclic Aromatic Hydrocarbons (PAH)

Sample #	Parameter	Mill	Influent Ozone Reactor	Effluent Ozone Reactor	Elimination Ozone Reactor	Effluent Biofilter	Elimination Biofilter	Elimination total
			ng/l	ng/l	%	ng/l	%	%
1	Naphtalin	LWC	<25	<25	n.a.	<25	n.a.	n.a.
1	Acenaphthylen	LWC	<15	<15	n.a.	<15	n.a.	n.a.
1	Acenaphthen	LWC	<22	27	increase	29	~0%	~0%
1	Fluoren	LWC	27	22	19%	<14	>36%	>48%
1	Phenanthren	LWC	321	99	69%	93	6%	71%
1	Anthracen	LWC	<11	16	increase	22	increase	increase
1	Fluoranthen	LWC	157	40	75%	45	-13%	71%
1	Pyren	LWC	40	11	73%	12	-9%	70%
2	Naphtalin	SC	<25	<25	n.a.	<25	n.a.	n.a.
2	Acenaphthylen	SC	<15	<11	n.a.	<17	n.a.	n.a.
2	Acenaphthen	SC	<16	9	>44%	38	increase	increase
2	Fluoren	SC	37	18	51%	<18	~0%	>51%
2	Phenanthren	SC	204	66	68%	51	23%	75%
2	Anthracen	SC	<9	15	increase	23	increase	increase
2	Fluoranthen	SC	90	33	63%	21	36%	77%
2	Pyren	SC	30	11	63%	8	27%	73%

Concentrations shown as <XX ng/l means that the results are below the Limit of Detection (LOD) at XX ng/l.

The reason for the high content of Phenanthren and Fluoranthren is not known. But it can be the resulting composition of the several types of “Carbon-Black” in the waste paper input.

A general elimination partly over 70% can be found. But at the concentration level of trace elements, the accuracy could be low. There is always a certain range in the precision of the results. This is also the explanation for the increased concentration of some substances during the AOP process, which is not explainable from chemical point of view.

4.2.3.6 Endocrine disruptors removal

Endocrine Disrupting Substances can be found in recovered paper and in wood. Endocrine disruptors are substances that may interfere with the organisms endocrine system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife. The measurement was performed during standard operation mode. The effluent of biological stage LWC is showing strong significant estrogenic activity even at a dilution of 1:12, the values for the other dilutions are also plausible. The result is given as an induction rate for the enzyme β-galactosidase (AiF 15181, (2009)). The induction rate of the almost undiluted sample of 3.5 (dimensionless) corresponds to the values, which can be found in other papermills, which are using mechanical pulp or recovered paper. Effluent ozone reactor and biofilter samples are almost identical. Therefore it was shown that the significant estrogenic potential has been significantly reduced by the oxidative ozone treatment, not by biological degradation in biofilter. In both samples an estrogenic potential has been determined only in the nearly undiluted sample, which is close to the detection limit for the induction rate of 1.5. All other dilutions show no estrogenic effect (see attached complete report as Annex 2).

4.2.3.7 Phthalate removal

Chemistry and Uses: Phthalates or phthalate esters (esters of phthalic acid) are mainly used as plasticizers (substances added to plastics to increase their flexibility, transparency, durability, and longevity). The mostly used phthalates are:

- Di(2-ethylhexyl)phthalat (DEHP)
- Di-isodecylphthalat (DIDP)
- Di-isononylphthalat (DINP)
- Dibutylphthalat (DBP)
- Di-isobutylphthalat (DIBP)
- Benzylbutylphthalat (BBP)
- Di(2-propylheptyl)phthalat (DPHP)

Harmful effects: Several phthalates are endocrine disruptors. Endocrine disruptors are chemicals that may interfere with the organism's endocrine system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife. Some phthalates are listed as a human carcinogen.

Relation to the paper industry: Phthalates are used in very thin plastic films. Some paper grades are laminated with these plastic films, to improve the resistance against water, grease or dirt. Phthalates are also components in printing inks. Therefore phthalates can be found in recovered paper and in the wastewater and sludge from a deinking plant.

Results: The concentration of phthalates in the influent and effluent of AOP has been below detection limit under normal operational conditions. Only two phthalates could be detected in SC wastewater (**Table 17** and Table 18).

Table 17**:** Phthalates in SC wastewater (below LOD)

Substance	Influent AOP wastewater LWC	Influent AOP wastewater SC µg/l
	µg/l	µg/l
Di(2-ethylhexyl)phthalat (DEHP)	< 1	< 1
Di-isodecylphthalat (DIDP)	< 5	< 5
Di-isononylphthalat (DINP)	< 5	< 5
Dibutylphthalat (DBP)	< 1	< 1
Di-isobutylphthalat (DIBP)	< 0,5	< 0,5
Diethyladipat (DEA)	< 0,25	< 0,25
Diethylphthalat (DEP)	< 0,25	< 0,25
Diethylhexyladipat (DEHA)	< 0,5	< 0,5

Concentrations shown as < XX ng/l means that the results are below the limit of detection at XX ng/l.

Table 18: Phthalates in SC wastewater

Sample #	Substance	Mill	Influent Ozon Reactor [µg/l]	Effluent Ozone Reactor[µg/l]	Elimination Ozone Reactor	Effluent Biofilter[µg/l]	Elimination total
			µg/l	µg/l		µg/l	
2	Benzylbutylphtalat (BzBP)	SC	0,21	0,27	none	0,21	none
2	Tri-n-butylphosphat	SC	0,11	0,13	none	0,12	none

No elimination was found. But at the concentration level of trace elements, the accuracy could be low. There is always a certain range in the precision of the results. This is also the explanation for the increased concentration of some substances during the AOP process, which is not explainable from a chemical point of view. The result might not be valid for higher concentrations of phthalate, which could be found in other papermills or industries.

4.2.3.8 Perflourinated compounds (PFC) removal

Perflourinated compounds are used in the paper industry for water, grease or dirt proofed papers. The compounds can be found in recovered paper. 11 typical PFT have been tested in wastewater from the LWC mill (including wastewater from the deinking plant). All values have been below detection limit (Table 19). The reason for this is the special recovered paper input at Plattling mill, which doesn't include any PFT containing paper grades.

Table 19: PFC in wastewater (below detection limit)

Substance	Influent AOP wastewater LWC	Influent AOP wastewater SC
	ng/l	ng/l
Perfluoroctansulfonat (PFOS)	< 16,7	< 16,7
Perfluoroctansäure (PFOA)	< 16,7	< 16,7
Perfluorbutansulfonat (PFBS)	< 25,0	< 25,0
Perfluorhexansulfonat (PFHxS)	< 25,0	< 25,0
Perfluorhexansäure (PFHxA)	< 16,7	< 16,7
Perfluorheptansäure (PFHpA)	< 16,7	< 16,7
Perfluoroctansulfonamid (PFOS)	< 16,7	< 16,7
Perfluornonansäure (PFNA)	< 16,7	< 16,7

Substance	Influent AOP wastewater LWC	Influent AOP wastewater SC
Perfluordecansulfonat (PFDS)	< 25,0	< 25,0
Perfluordecansäure (PFDeA)	< 16,7	< 16,7
Perfluordodecansäure (PFDoA)	< 16,7	< 16,7

Concentrations shown as <XX ng/l means that the results are below the Limit of Detection at XX ng/l.

4.2.3.9 Coloring substances removal

The typical color of biological treated wastewater from papermill is a dark reddish brown. The main sources for the brown color are dissolved lignin and resins from peroxide wood bleaching. Additionally some slightly red coloration could come from wastewater from the deinking plant. The coloring substances are not harmful to human beings. But the color is visible in the receiving river and affects the conditions of the river.

The discoloration curve is shown in **Figure 42**.

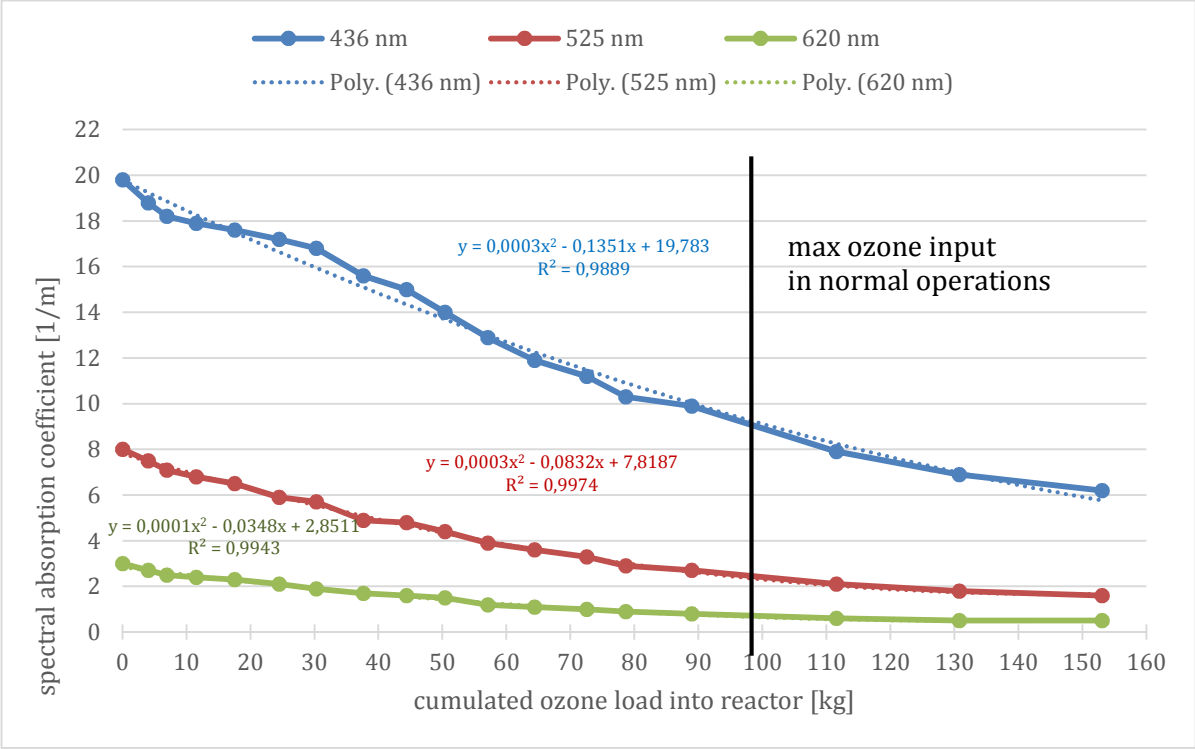

Figure 42: Discoloration of LWC versus cumulated ozone load wastewater

The discoloration was determined at 3 different wave lengths (ISO 7887). All 3 wave lengths are in the visible range of light and can be used to describe the discoloration of the effluent.

Figure 43: Discoloration of LWC wastewater

Sample B15 / B16 show the results which we gained under normal operation mode. B18 shows the result with maximum retention time in the batch test. The result of this test demonstrates that treatment with ozone is a very efficient method for discoloration of papermill wastewater. This technique has already been implemented in a speciality paper-producing papermill.

4.2.4 Ozone diffusion performance test in fresh water

Although the ozone diffusion performance test in fresh water is no standardized method according to DIN standards or adequate until today, it was decided to investigate the ozone diffusion capacity of the ozone diffusion system by a new approach.

Theoretical background for the investigation of the ozone diffusion performance was the consideration that ozone as the strongest oxidation agent likely reacts quantitatively in the complex wastewater matrix. However, according to the task, which is the creation of predominantly interface reaction conditions in order to achieve the accumulation of biodegradable compounds by partial oxidation while minimizing the complete oxidation as described in chapter 2.4.3, the mixing and distribution efficiency of the diffusion system should be controlled. The full involvement of ozone over a large surface area on the one hand and full utilization of ozone without loss of ozone into the gas phase should be ensured with wastewater in a reactor prior to commissioning.

Two possible ozone diffusion performance tests for verification of the ozone diffusion transfer capacity implemented in the ozone injector / diffusion system are applicable according to the present experiences.

a. The oxygen transfer capacity test in pure water according to the „DWA-Merkblatt M209 or DIN EN 12255-15“ as an absorption method and the indirect calculation of the ozone transfer by an estimated diffusion coefficients

and

b. The indigo full discoloration method in a large-scale batch test after separation of one reactor and a refilling with fresh water [Bader, Hoigné (1981)], [Yates, Stenstrom (2000)], [DIN (2011)].

The selected ozone diffusion performance test was the indigo full discolorisation method as proposed and executed by the „Technische Universität München, Institut für Wasser und Umwelt, Lehrstuhl für Siedlungswasserwirtschaft“.

Basis of the measurement method is the discoloration of indigo carmine by ozone in a stoichiometric reaction. Indigo carmine ($C_{16}H_8N_2Na_2O_8S_2$) in technical quality with a real component of ≥ 80% was used. The decrease in absorbance is measured at a wave length of 610 nm. The method is based on a difference measurement.

The reason for the selection of the indigo discoloration method is the precondition that the ozone consumption can be determined by a stoichiometric reaction of ozone and therefore provides more precise results than the calculation method (which has to be verified).

Figure **44** shows the results of the ozone transfer capacity in fresh water at different set points for the ozone generator.

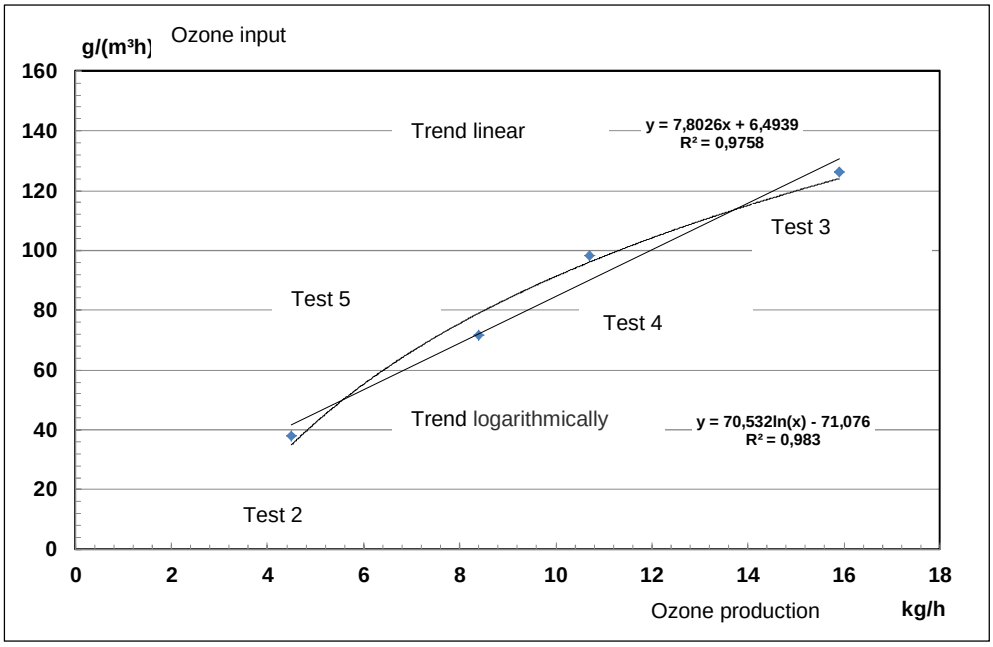

Figure 44: Determined ozone transfer dependent on the theoretical ozone generator set-point generation

Figure 44 shows the measured ozone diffusion by difference measurement between the individual set points and the produced ozone quantity, which is measured by online data evaluation by the main process control system (PCS). The measured ozone transfer capacity according to the report amounts to between 38 and 126 g/(m³h). The different measurement points (difference in concentration, time and reactor volume) are correlated to the ozone production, which is online measured in the PCS. The ozone consumption according to Figure 44 is equivalent to 69 % compared to the given theoretical ozone generator set point.

The results according to the indigo full discoloration method provide an insufficient ozone transfer capacity in the batch test. However, the result is in contradiction to the measured high-efficient ozone utilisation according to Figure 11 and the statistically verified operational data. Further clarification is required from the research point of view.

Unfortunately the verification of the large-scale ozone diffusion performance test could not be anticipated due to a lack of time within this project.

The reasons for the deviation of the results between the indigo discoloration test compared to the achieved regular statistically evaluated operational results (see Figure 19) are summarized below:

- The higher quantity of secondary ozone oxidation reactions deviating from the chemical stoichiometric reaction assumptions

- The influence of an insufficient cleaning of the ozone reactor in the batch test after operation with wastewater, which leads to an additional consumption of organic material on the surface in the water submerged area of the reactor

- The hydraulic influence of the batch test conditions without wastewater flow compared to the counter current in normal operation

However, the ozone diffusion performance test provides important information about the applicability of the available tests. Further R&D is required for the development and clarification of the appropriate ozone diffusion performance test in fresh water.

Figure 45 shows the diverse different photometric measured cuvettes for discoloration during the indigo method.

Figure 45: Photometric measured cuvettes for discoloration during the indigo method test

5 Environmental balance AOP

5.1 Best Available Technique (BAT) and BREF

With implementation of the *Directive for Integrated Pollution and Prevention Control (IPPC)* in national legislation for EU member states, the application of the “best available techniques” (BAT) to prevent and reduce environmental emissions from industrial installations became the “permission prerequisite” for industrial plants in Europe [EG (2008)]. The system applies the principle that environmental influences are no longer judged separately from emissions to different environmental media air, water and ground. The evaluation (appropriately also the requests) and avoidance measures have to be evaluated in an integrated approach, regarding the influence on all the environmental media (cross-media effects) [BREF, 2013].

Also the following industrial emissions directive (IED) follows this approach. Any legal permit for industrial installations has to reflect the result from the European information exchange process on Best Available Technique (BAT) as described in the Best Available Technique Reference Documents (BREF). Any emissions limit value in a legal permit has to ensure that the associated emission and consumption levels published in the Conclusions on Best Available Techniques (BATC) for the relevant industrial sector are met in the individual installation [BATC (2014)].

The BATC provide information about the effluent quality to be expected when an effluent treatment plant representing the best available technology is operated. For the production of these type of paper grades in BATC Nr. 50, this is generally a two-stage biological treatment plant, where the different stages are characterized by different micro biotic communities (biocenosis). Such a system, comprising a film reactor followed by an activated sludge reactor, without a settler between the stages, is a classical two-stage system.

There are several reasons for this development beside the main reason to further increase the COD reduction another important reason is to avoid bulking sludge in the final activated sludge treatment stage. To a limited extent this could be achieved in single stage activated sludge reactors using either selector tanks or the aeration cascade configuration. This was tried at the Plattling mill first, but despite success, the results were only satisfactory for a short period. Other reasons for using two-stage systems reduce production area and sometimes lower investment costs.

Advanced treatment of papermill wastewater, applied to eliminate organic substances beyond the effect of mechanical and biological cleaning, is increasingly demanded to protect the receiving waters.

6 Technical comparison of conventional advanced treatment processes with AOP considering techniques described in the BREF document

Advanced wastewater treatment is needed, when the concentration of COD or other pollutants are still too high for the receiving water, even after an adequate two-stage biological treatment.

Generally speaking, advanced treatment processes may be applied optionally either before or after biological effluent treatment. For all processes that have undergone proven operational tests in pulp and papermills, it may safely be stated that – unless partial flows can be successfully treated – advanced treatment stages implemented after the biological treatment are most economical and effective. Only these processes are discussed here.

The following processes are used as tertiary stages for advanced treatment of papermill wastewaters:

a) Tertiary wastewater biofilters (BREF chapt. 2.9.11.3.1)

b) Membrane processes (ultrafiltration, nanofiltration, reverse osmosis) (BREF chapt. 7.3.3)

c) Evaporation

d) Chemical precipitation (BREF chapt. 2.9.11.3.1; 7.3.12)

e) Advanced oxidation processes (AOP) (BREF chapt. 6.3.9)

Sandfilters and polishing ponds following the secondary treatment are not considered to be advanced treatment, since they only have a substantial additional treatment function when the secondary stage does not work properly.

Membrane processes as well as evaporation (followed by condensation) of the effluent are technical possibilities for advanced treatment, which, until now, could not gain acceptance for different reasons. The high operation costs and energy required are a disadvantage of both types of processes. Fouling, blocking and ageing problems of the membranes, which are not solved yet satisfactorily, are a drawback for the membrane processes.

A completely unsolved problem in papermills (generally not so in pulp mills) is the question what to do with the concentrated extracts of evaporation or the concentrate of membrane processes. Still in regions (e.g. in Spain, India and Israel) with water scarcity these techniques are further investigated and implemented in certain installations.

The process d), precipitation and coagulation, as applied with the existing DAF system, is examined in chapter 7.1.2.

The process according to e), AOP as implemented at the MD Papier GmbH papermill in Plattling has gained a high reputation whenever the elimination achieved in a tertiary biofilter is not sufficient. Therefore AOP in most cases is the process of choice. The efficiency of the process depends on the optimum ozone dosage in order to achieve maximum BOD/COD ratio or, with other words, best possible biodegradability (see Figure 18). Once this is achieved, maximum COD elimination in the subsequent biofilm reactor will result in the lowest operation costs and a far reduced cross-media effect concerning energy and LOX consumption.

The environmental and cross-media aspects for process e) AOP are examined in detail in the following chapters.

6.1 Environmental benefits of AOP

The optimization of an existing WWTP and a downstream implementation of AOP ensure that the treated effluent fulfills the requirements in sensitive FFH areas for the protection of the receiving water (as in the case of the papermill MD Papier GmbH, Plattling located close to the river Isar).

The basic effect of partial oxidation in the combination of ozone plus wastewater biofilters in which persistent COD becomes biodegradable can be further improved with the designed innovative two-stage depressurized ozone reactor and biofiltration (see cross-media evaluations in the following chapter 4.4).

For an economic efficient performance one main objective is to optimize (reduce) the specific ozone consumption for the overall COD to be eliminated by AOP. A reduction of the specific ozone consumption related to the eliminated COD, and at the same time an improved energy efficiency complemented by minimized operation costs for energy and LOX are expected.

Apart from the enhanced COD-removal, a far-reaching elimination of AOX, color and other disturbing substances like complexing agents (EDTA and DTPA) and micro pollutants is achieved simultaneously in most cases with less ozone.

The implementation of the optimized AOP concept, instead of a large extension of the existing chemical storage and dosing system and an additional DAF system - which was an examined technical solution for the papermill as well - resulted in a far-reaching reduction (instead of a considerable increase) of predominantly inorganic tertiary sludge and salt input in the effluent prior to discharge.

7 Examination of the cross-media effects AOP

7.1 Specific data and cross-media evaluations in comparison to BAT/BREF

Until electrical power is produced from green energy sources, the energy consumption for the ozone generation and ozone diffusion systems, as well as the consumption of LOX, (which is produced by an air separation plant to liquified oxygen (LOX) using valuable energy as well) has to be considered for cross-media effects.

In addition to the new AOP at MD Papier GmbH in Plattling and according to current information available, the following large-scale advanced oxidation systems for wastewater treatment in the pulp and paper industry have been installed during the last years and might be considered for a comparison of overall environmental performance:

- SCA Laakirchen (tertiary effluent treatment, with ozonation for reduction of COD peak emissions), AT;
- Myllykoski Lang Papier Ettringen (tertiary effluent treatment, with ozonation for COD load reduction), DE;
- Papierfabrik Gmund (ozonation for decolorisation of process water before discharge and partial recirculation), DE;

Note: Other advanced oxidation systems might be installed in papermills in other European countries using ozone and biofiltration technology as well, but published information is currently not available.

The plant at the **papermill in Gmund** has no tertiary treatment and performs a further treatment using ozone (mainly for decolorization).

The AOP at the **papermill Lang Papier in Ettringen** is out of operation for several years. In the meantime, different paper grades are produced and treated. Up to now, the effluent quality according to the existing WWTP requires no tertiary effluent treatment. According to the published information the ozone consumption, after the AOP went into operation, was significantly higher compared to earlier pilot tests. It is further referred by the experts from Lang Papier, that the reasons for the different results might be a modified bleaching within the stock preparation, a higher specific water consumption as well as a different biological treatment in the WWTP compared to the results gained during the pilot testing. We have no further published information or confirmation of these assumptions.

Operational costs of a plant according to [BREF (2013)], [Schmidt, Demel, Lange, (2001)] are given with 0.3 – 0.4 €/m^3 of treated effluent. The specific costs related to the wastewater flow are above the costs of the reference plant and of the AOP at MD Papier GmbH in Plattling (see economic analyses below). However, the cost positions for the calculation basis and specific costs related to COD eliminated or gross production are not included in the BREF documents or published data. Due to the missing information it was not possible to include Lang Papier in the benchmark evaluations.

Detailed and valuable information are published by [Kaindl (2006)], [Kaindl (2009)] for the papermill in Laakirchen, AT. These available data are taken as reference data in comparison to results of the AOP at MD Papier GmbH in Plattling. The AOP in Laakirchen is in full operation. The specific cross-media data are given in [BREF chapter 6.3.9] and mainly refer to the published data of [Kaindl (2009)] as well.

The comparison of the main technical and cross-media evaluations of the AOP at MD Papier GmbH, Plattling with the reference data according to [Kaindl (2006), (2009)] and [BREF (2013)], [BATC (2014) are summarised in Table 20 **- Table 23**.

The main design and technical data compared with the reference data are summarised in Table 20**.**

Table 20: comparison of reference data AOP; design and technical data

MD Papier GmbH, Plattling				**Reference data**	
(statistical data evaluation August 2013 until October 2014; see also Table 3, **Fehler! Verweisquelle konnte nicht gefunden werden.** - Annex 1, Table F)				[BREF (2013)]	[KAINDL (2009)]
Parameter	dim.	value		value	value
Daily COD load elimination, design	kg/d	**1,320** *(mv+2s)*			**1,830**
Specific ozone consumption per COD inflow, design	kg/kg	**-**			**0.29**
Specific ozone consumption per COD eliminated, design	kg/kg	**< 1.0** *(mv+2s)*			
Specific ozone consumption per COD eliminated, project objective	kg/kg	**0.40 – 0.60** *(mv-2s/mv+2s)*			
Capacity ozone generator	kg/h	**55**			**75**

MD Papier GmbH, Plattling				Reference data	
(statistical data evaluation August 2013 until October 2014; see also Table 3, **Fehler! Verweisquelle konnte nicht gefunden werden.** - Annex 1, Table F)				[BREF (2013)]	[KAINDL (2009)]
Ozone concentration after ozone generator	wt.-%	**10**			**12**
Efficiency ozone diffusion system design	%	**> 95**			**98**
Operation pressure ozone reactor (absolute)	bar	**1**			**3**
Type of cooling for ozone generator (chiller or cooling water)	-	*cooling water (fresh water)*			*cooling water (fresh water)*
HRT ozone reactor total	h	**0.4** (two stages)			**0.08** (one stage)
Spec. hydraulic surface load biofiltration	m^3/m^2h	**6.5**			**6.5**
Filter media height	m	**3.0**			**2.0**

Table 20**:** The AOP at MD Papier GmbH is designed as a two-stage depressurized ozone reactor operated at atmospheric pressure and higher HRT (see also Table 3) compared to the reference plant, which is designed as a one-stage pressurized ozone tank operated at approx. 3 bar. Using pressurized ozone reactors the volume of the ozone reactors can typically be reduced in the large-scale application. The reason is that the ozone reaction is transferred predominantly to the bulk and needs therefore much less volume compared to the film reaction, where the ozone predominantly reacts in the film by diffusion from an ozone bubble (bubble column which needs more volume) to the film (see chapter 2.4.3.1.). The HRT of the ozone reactor in the reference plant is therefore reduced while the HRT in the depressurized system is extended.

The hydraulic surface load of the biofiltration stage is identical. The biofilter height at MD Papier GmbH is 3 m compared to 2 m at the reference plant, which results in an increased volume of approx. 33 %. A lower BOD load related to the total volume of the biofllters is achieved and a lower BOD volume loading exists (higher capacity for biodegradation of organic compounds from the ozone reactors).

The ozone generation of the reference plant is designed for 12 wt.-% of ozone in the carrier gas (LOX) compared to 10 wt.-% at MD Papier GmbH. This leads to a higher absolute LOX consumption at MD Papier GmbH. However, it is technically possible to generate an ozone concentration e.g. up to 16 wt.-% but at the same time specific energy for the generation increases. The optimal condition between more energy for ozone generation (and higher energy costs) and less LOX consumption (and less LOX cost) or vice versa has to be examined case by case (local costs for energy and LOX, reliability and life time e.g. for the dielectrics (see chapter 3.6.5) etc.). LOX for ozone generation is not produced on site but is delivered on demand by an industrial gas company. Further information about the electrical energy consumption and cross-media evaluations concerning the requirement of LOX are given in the following Table 16 – Table 21: comparison of reference data AOP; specific ozone consumption and ozone diffusion efficiency

Both plants are using fresh water for cooling the ozone generator instead of a chiller system (which means a reduced specific electrical energy consumption of approx. 4.5 kWh per kg of ozone produced in both cases).

The offgas of the ozone reactors at MD Papier GmbH is recompressed and used for oxygen supply to the aerobic high-loaded stage of the WWTP. No ozone offgas destruction is needed. The savings in the specific energy consumption amount to approx. 0.3 kWh per kg of ozone produced.

The results of the specific ozone consumption and of the ozone diffusion efficiency compared to the reference data are shown in Table 21: comparison of reference data AOP; specific ozone consumption and ozone diffusion efficiency

. Table 21: comparison of reference data AOP; specific ozone consumption and ozone diffusion efficiency

MD Papier GmbH, Plattling				**Reference data**	
(statistical data evaluation August 2013 until October 2014; see also Table 3, **Fehler! Verweisquelle konnte nicht gefunden werden.** - Annex 1, Table F)				[BREF (2013)]	[KAINDL (2009)]
Parameter	dim.	value		value	value
COD load eliminated during ozonation	kg/d	**966** *(mv)* **469 – 1,463** *(mv-2s/mv+2s)* **1,520** *(max)*			

MD Papier GmbH, Plattling				**Reference data**	
(statistical data evaluation August 2013 until October 2014; see also Table 3, **Fehler! Verweisquelle konnte nicht gefunden werden.** - Annex 1, Table F)				[BREF (2013)]	[KAINDL (2009)]
Parameter	dim.	value		value	value
Specific ozone consumption per COD eliminated	kg/kg	**0.90** [1)] *(mv)* **0.46 – 1.35** *(mv-2s/mv+2s)* **0.76** [2)] *(mv)* **0.45 – 1.06** *(mv-2s/mv+2s)*			**0.4 – 2.3** *(results of pilot tests)*
Ozone generation	kWh/kg O_3	**7.75** [3)] *(mv)*		**10 - 13**	**14** [3)]
Ozone system (except ozone generation)	kWh/d kWh/m³ kWh/kg ozone	**3,435** [4)] **0.33** **3.95** *(mv)*			
Pumps ozone system at design flow	kWh/m³	**0.17**			
Pumps ozone system	kWh/m³				**0.27**
AOP (ozone generation 10 wt.-% ozone and diffusion system)	kWh/kg ozone	**11.69**			
For information only: AOP (ozone generation 10 wt.-% incl. LOX and diffusion system)	*kWh/kg ozone*	*11.63+6.38* [5)] *= 18,06* [6)]			
Ozone efficiency diffusion system operation achieved	%	**99.73** *(mv)* **97.65 – 100** *(mv-2s/mv+2s)*			

[1)] specific values referring to all data; until April 2014 only grab samples are taken from the in- and outflow of the AOP stages; since May 2014 the data evaluation bases on 24 hrs composite samples

[2)] specific values referring to 24 h composite samples since beginning of May 2014

[3)] the electricity consumption for LOX production is not included

[4] ozone diffusion system, cooling water pumps, offgas compressor (only raw water pumps to AOP are not considered*)*
[5] benchmark information according to [EIGA (2010)]; 638 kWh/t LOX (corresponds to 0.638 kWh/kg LOX or 6.38 kWh/kgO_3 generating ozone with 10 wt.-% including LOX)
[6] calculated value according to [5] for information only

Table 21: comparison of reference data AOP; specific ozone consumption and ozone diffusion efficiency

: Reference data for comparison of the specific ozone consumption differentiated in ozone generation and ozone diffusion as well as for the efficiency of the ozone diffusion system are not available.

The average specific ozone consumption according to the evaluated data since beginning of May 2014 amounts to 0.76 kg ozone per kg of COD eliminated. The objective to reach a specific ozone consumption in the range of 0.4 – 0.6 kgO_3/kg COD_{elim} was not achieved within the testing period. However, the optimization of the AOP at MD Papier GmbH is not finalized. Three values are found below 0.6 kgO_3/kg COD_{elim} (see Figure 16, Figure 17 and notes). Further improvements are expected within the required optimization measured as described in chapter 5.

The specific energy consumption for production of ozone seems much more efficient for the ozone generation at MD Papier GmbH (mv 7.75 kWh per kg of ozone compared to 14 kWh per kg of ozone related to the reference data, both values without the electricity consumption for the production of LOX). An evaluation of the electricity consumption inherent in the production of oxygen using best available air separation technology needs to be differentiated according to the form of the delivered product, whether liquid or gaseous (compressed). A benchmark information is published in [EIGA (2010)] (see data Table 19, note 5).

However, the database in the BREF considers no statistical evaluations. The statistically evaluated AOP operation data at MD Papier GmbH therefore cannot be directly compared with the data given in the BREF.

The ozone diffusion into the two-stage ozone reactors at MD Papier GmbH is very efficient and nearly complete (see Table 16, ozone efficiency mv 99.7 % and Figure 11). Reference data for comparison are not available to us.

Cross-media evaluations concerning the energy consumption related to the eliminated COD are shown in Table 22.

Table 22: cross-media evaluation AOP; energy consumption related to COD eliminated

MD Papier GmbH, Plattling				**Reference data**
(statistical data evaluation August 2013 until October 2014)				[BREF (2013)]
Parameter	dim.	Value *(mv)*		Value *(annual average)*
Biological treatment	kWh/kg $COD_{elim.}$	**0.76** 1)		**1.5** *2)*
Ozone treatment	kWh/kg $COD_{elim.}$			**20.8** 4)
AOP	kWh/kg $COD_{elim.}$	**11.35** 3)		
For information only: AOP including LOX	kWh/kg $COD_{elim.}$	*18,06 5) * 0.76 6) = 13.73 7)*		
Oxygen (LOX) consumption for ozonation	kg LOX/kg $COD_{elim.}$	**9.17**		**7.9**
1) WWTP including freshwater pumping station, primary treatment, cooling, biological treatment and secondary clarification, DAF, sludge treatment, chemical storage and dosing (ventilation / air conditioning / common area electricity are not considered)				
2) the WWTP stages for determination of the energy consumption are not specified in the BREF				
3) Energy for LOX production is not included				
4) The electrical consumption for ozone generation according to BREF is given without the electrical energy requirement for LOX (see Table 19, note 3). No specific energy data are found for the LOX production in the BREF nor in the reference plant. We have therefore presumed as a consequence, that the data given do not include the energy requirement for LOX as well.				
5), 6), 7) calculated value for information only; 5) see Table 19 note 6); 6) see Table 19 note 2				

Table 22**:** the specific energy consumption for the WWTP at MD Papier GmbH related to the eliminated COD is lower by 49 % compared to the reference data set as 100 % (see data above 0.76 related to 1.5 kWh/kg$COD_{elim.}$).

For the AOP at MD Papier GmbH the specific energy consumption related to the eliminated COD is lower by 45 % compared to the BREF data (see data above 11.35 related to 20.8 kWh/kg$COD_{elim.}$). The estimated total specific energy consumption related to the eliminated COD amount including the published benchmark information for the energy requirement for LOX [EIGA (2010)] amounts to 13.7 kWh per kg of COD eliminated.

The far lower specific energy consumption of the AOP at MD Papier GmbH related to the eliminated COD indicates a (significant) overall better energy efficiency.

The reasons can be found in:

- an efficient chemical reaction of ozone in the two-stage reactor and partial oxidation of persistent organic compounds
- a nearly complete utilisation of ozone within the diffusion system
- an efficient biochemical elimination of biodegradable compound after ozonation in the upstream biofilters
- an ozone generation latest technology

The specific LOX consumption related to the eliminated COD is higher by 16.5 % compared to the reference data (see data above 9.17 related to 7.9 kg LOX/kg $COD_{elim.}$). This results from the lower ozone concentration for the ozone generation in the AOP at MD Papier GmbH (10 wt.-% instead of 12 wt.-% for the reference plant) and the higher specific LOX requirement.

Cross-media evaluations concerning the energy consumption related to the gross paper production are shown in Table 23.

Table 23**:** cross-media evaluation AOP; energy consumption related to gross paper production

MD Papier GmbH, Plattling				**reference data**
(statistical data evaluation August 2013 until October 2014)				[BREF (2013)]
Parameter	dim.	Value *(mv)*		Value *(annual average)*
Biological treatment	kWh/t paper gross	**13.66** *(mv)*		**18.9**
Ozone treatment	kWh/t paper gross			**7.5**
AOP	kWh/t paper gross	**3.24**		
Oxygen (LOX) consumption for ozonation	kg LOX/ t paper gross	**4.08**		**2.8**

Table 23: the lower specific energy consumption and the higher specific LOX consumption related to the eliminated COD as shown in Table 17 is reflected analogous if the gross production is taken as the reference basis.

However, a detailed interpretation of absolute values between MD Papier GmbH and the reference plant requires a detailed analysis of the production processes and paper grades produced and the resulting specific wastewater emission. Such information is confidential and could not be used within this project.

Cross-media evaluations concerning the final COD discharge to the receiving waters are shown in **Table 24**.

Table 24: cross-media evaluation AOP; specific COD discharge to receiving waters

MD Papier GmbH, Plattling				**reference data**
(statistical data evaluation August 2013 until October 2014)				[BREF (2013)]
Parameter	dim.	value		value
Emission standards for specific COD discharge (integrated mechanical pulping plant)	kg COD/t max. production	**3.0** 1) **up to 5.0** 2) **3.0** 3)		**0.9 – 4.5** 4) **up to 8.0** 5)
Achieved specific COD discharge related to German minimum requirements	kg COD/t max. production	**2.7** 6) *(mv+2s)*		
Specific COD discharge related to BREF	kg/t paper gross	**2.5** 7) *(mv)*		

1) about 95-percentile value related to maximum production capacity, based on daily 2 hrs samples or qualified grab sample (German Standards (so called minimum requirements)

2) in the case of bleached mechanical or deinked pulp (more than 50 % of fiber in final paper), as in the case of MD Papier GmbH, Plattling

3) water-legal permission for the direct discharge to receiving waters river Isar at site MD Papier GmbH, Plattling

4) yearly average related to the actual gross production

5) in the case of highly bleached mechanical pulp (70-100 % of fiber in final paper)

6) based on daily 2 hrs samples and related to max. production capacity

7) based on daily 2 hrs samples and related to gross production capacity (note: the gross production at MD Papier GmbH is available as monthly values; the monthly value is divided by the numbers of days per month and is then divided by the daily COD-load in the total outflow)

Table 24: It has to be kept in mind that in the EU member states very different ways of legislative regulations regarding emissions and consequently different ways of monitoring are applied. Therefore, in most cases it is not possible to compare national standards with the BAT values in a proper way [Möbius (2006), (2010)].

For German and Austrian Standards (so called minimum requirements) the specific COD discharge in kg/t COD is related to an almost maximum level (their level is not statistically defined, but it is about 95th percentile) and to a maximum production capacity of absolutely dry paper.

The specific COD emission values according to BAT are expressed as yearly average values related to the actual production, which allows much higher emissions than the German minimum requirements. The values themselves cannot be compared without reflecting the reference conditions.

The achieved specific COD discharge related to the German minimum requirements amounts to 2.7 kg/t and to 2.5 kg/t related to BREF conditions which represents quite a good compliance in this case. As mentioned in the notes to Table 19, daily production data were not available and monthly production data divided through the number of days per months has been taken as the basis. Higher variations might be expected when daily production data are used.

7.1.1 Economic analyses of AOP in comparison to BAT/BREF

The operational costs of the AOP depend to a large extent on the targeted COD reduction when ozonation is required. It is less informative to express the specific operation costs per m^3 of treated effluent, as the ozone consumption depends exclusively on the organic substance to be removed by chemical/biochemical oxidation. It is therefore more meaningful to report operational costs related to the COD load eliminated. The costs are based on the 2013/2014 production and the specific COD reduction as described in the previous chapters. The following data on operational cost give an impression of the order of magnitude of the costs based on the actual costs for energy and oxygen in 2014. However, the cost data basis for the specific energy and oxygen costs is quite different compared to reference data according to [BREF (2013)]. Additional calculations are done using the specific costs for energy and oxygen according to the reference data in order to enable the comparison.

The results of the economic analyses relating to the eliminated COD are shown in Table 25

Table 25: Economic analyses; specific operation costs related to COD eliminated

MD Papier GmbH, Plattling				**Reference data**
(statistical data evaluation August 2013 until October 2014)				[BREF (2013)]
Parameter	dim.	value		value
Biological wastewater treatment	€/kg $COD_{elim.}$	**0.09** 1)		**0.27** 2)
Ozone + biofilter	€/kg $COD_{elim.}$			**1.33**
AOP	€/kg $COD_{elim.}$	**1.64** 1) **1.37** 2) **1.14** 3) **0.95** 4)		
*1) Chemicals (DAF, sludge dewatering), nutrients, electrical energy (without sludge utilization); staff for operation and maintenance **is not included***				
*2) utilities (not specified), staff for operation and maintenance **is included**)*				
1) related to energy and LOX costs 2014 at MD Papier GmbH, Plattling				
2) related to energy and LOX costs 2014, data since May 2014 related to 24 h composite samples				
3) related to energy and LOX costs as mentioned in [BREF (2013)] and [KAINDL (2009)]				
4) related to energy and LOX costs BREF, data since May 2014 related to 24 h composite samples)				

Table 25: The specific operation costs related to the eliminated COD amount to 1.64 € per kg COD eliminated based on specific energy and LOX costs in 2014 compared to 1.33 € per kg COD eliminated based on older (and lower) specific costs according to [BREF (2013)]. Some cost information can be found in [KAINDL (2009)]. If the operation cost calculations are done with the specific costs mentioned there, the specific operation costs amount to 1.14 € per kg COD eliminated for die AOP at MD Papier GmbH, Plattling, which is lower by approx. 14 %. If the calculations are done based on the operation data since May 2014 when 24 h composite samples were taken at the outflow AOP as well, specific costs below 1,0 € per kg of COD eliminated might be expected. More data are required for verification.

The lower specific operation costs related to the eliminated COD reflect the overall more energy efficient process, as previously shown (see results in Table 21: comparison of reference data AOP; specific ozone consumption and ozone diffusion efficiency

The results of the economic analyses relating to the gross paper production are shown in Table 26.

Table 26: Economic analyses; specific costs related to gross paper production

MD Papier GmbH, Plattling				**Reference data**
(statistical data evaluation August 2013 until October 2014)				[BREF (2013)]
Parameter	dim.	value		value
Biological wastewater treatment	€/t paper gross	**1.43**		**3.7**
Ozone treatment	€/t paper gross			**0.53**
AOP	€/t paper gross	**0.75** *1)*		
AOP	€/t paper gross	**0.52** *2)*		
1) related to energy and LOX costs 2014				
2) related to energy and LOX costs BREF				

Table 26: The specific operation costs related to the gross paper production are higher for the AOP at MD Papier GmbH, Plattling, when the actual higher specific costs for energy and oxygen are considered (see notes under Table 20). More or less the same range of specific costs is achieved when the specific operation costs related to BREF are considered (see 0.52 € per t of paper gross for the AOP at MD Papier GmbH, Plattling compared to 0.53 € per t of paper gross related to BREF).

The interpretation of this result is that more COD was eliminated on an absolute base during the chosen period which compensates the lower specific operation costs related to the eliminated COD, as found in Table 20.

7.1.2 Cross-media evaluations in comparison to the existing DAF

As mentioned in chapter 1.2, the COD (load and concentration) can be decreased by precipitation and flocculation using a huge amount of trivalent metals (typically as aluminium (Al^{3+}) or iron (Fe^{3+}) salts in water treatment processes) and separation of the resulting sludge by DAF.

Alum (aluminium sulphate solution as $Al_2(SO_4)_3$ x $14H_2O$ with 14 % active substance), which as a chemical additive in the papermaking process is used for chemical dosing in DAF system as well.

The experiences in DAF operation show that a surplus of Alum and polymer dosing is necessary in order to achieve an efficient tertiary sludge removal and to compensate the daily fluctuation in wastewater characteristics, which finally depend on

- the wood quality and season of the year
- the intensity of the mechanical pulp bleaching (more intensive bleaching is usually required in the summer months, less in the winter months)
- the paper grades

and

- the efficiency in the biological wastewater treatment before tertiary treatment in the DAF.

Following dosing concentrations related to the wastewater quantity are applied in operation:

- Approx. 50 – 90 mg/l as Al^{3+} (average approx. 60 mg/l)
- Approx. 500 – 900 mg/l $Al_2(SO_4)_3$ x $14H_2O$ as dry substance
- Approx. 3 mg/l of polymer as flocculation additive
- PH-adjustment with caustic soda, if required

Alum and polymer are dosed flow proportional to wastewater flow. In addition, the formation of stable flakes must be controlled to reach a concentrating sludge layer (flotate sludge) for an efficient mechanical separation. Flotate sludge of approx. 25 – 40 g/l (2.5 – 4.0 wt.-%) as dry matters is achieved in operation. The suspended solid concentration outlet DAF is below 15 mg/l under the condition that stable precipitation conditions and a sufficient mechanical flotate removal are achieved.

Mainly inorganic aluminum hydroxide ($Al(OH)_3$) and the part of precipitated organic substances result as precipitation sludge in the DAF. According to the alum dosing as mentioned above the following quantity of tertiary sludge result:

- Approx. 145 – 260 mg/l as $Al(OH)_3$ (average approx. 170 mg/l)

- Approx. 1.0 kg sludge as dry matter per kg COD eliminated (average)

The COD removal efficiency ranges from 10 up to 55 % (average approx. 30 – 35 %) in the practical operation.

The salt content increases by the sulphate input (or by chloride if Me(III)-chloride salts are applied) in the wastewater. Approx. 200 – 300 mg/l of sulphate $(SO_4)^{2-}$ from alum is dissolved in the effluent according to the dosing concentration as mentioned above. Approx. 1 – 3 mg/l of soluble aluminum (Al^{3+}) is discharged in addition with the effluent in case of a relevant surplus of alum or at suboptimal pH conditions [Höke, Balzer, Wanjek (1996)].

The composition of the papermill effluent generally requires the addition of nitrogen and phosphorus as nutrients necessary for the growth of microorganisms (phosphoric acid and urea are utilized as phosphorous and nitrogen source). Nutrients have to be dosed in such a quantity that nitrogen (as ammonia $N\text{-}NH_4$) and phosphorous (as ortho-phosphate $P\text{-}PO_4$) at the outlet of the secondary clarifier are kept in the range of 0.5 – 1.0 mg/l to ensure a sufficient nutrient supply for biodegradation of organic substances in the biological treatment. A phosphorous elimination of approx. 50 % might be expected in the DAF by phosphorous precipitation together with the precipitation of organic substances. However, the discharge limit for phosphorous elimination of 1.5 mg/l (as P_{total}) and nitrogen (as N_{total}) of 8.0 mg/l is ensured already at the outlet of the secondary clarifier of the WWTP.

The considerable amounts of tertiary sludge and the additional salt release are contrary to the COD and phosphorous removal by precipitation and separation by DAF. Focus of the operation is reliable and stable precipitation and sludge separation in the DAF. Specific cross-media calculations of the energy consumption related to the eliminated COD or to the gross paper production are difficult (surplus of dosing chemicals) and can only be examined on a case by case basis. A before and after comparison of specific cross-media data of the DAF is not considered in this project. However, no changes of the specific cross-media data in the DAF before and after are expected.

One of the main objectives is an extensive reduction of the tertiary sludge quantity in order to reduce the part of the mainly inorganic tertiary sludge for utilization by composting.

The development of the tertiary sludge amount before and after operation of the AOP is shown in **Figure 46**.

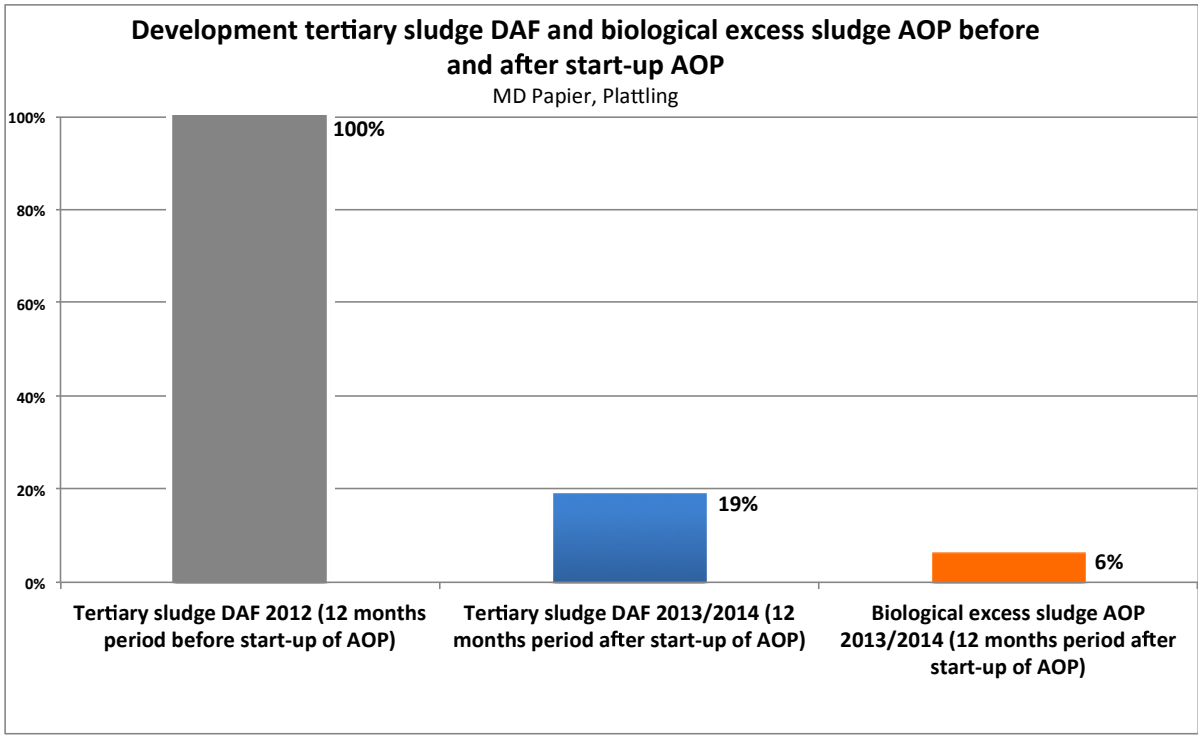

Figure 46: tertiary sludge DAF before and after operation of AOP

The data in this figure serve to demonstrate of the expected sludge amount before and after the operation of the AOP. Quantitative figures are given below. The sludge concentration is not measured by daily analyses either in the tertiary sludge from DAF or in backwash water of the biofilters and is considered therefore by typical or specific data. However, the tertiary sludge flow from the DAF to the sludge dewatering is measured by an inductive flow meter. The tertiary sludge amount is calculated with a tertiary sludge concentration of 35 g/l. The biological excess sludge of the AOP is calculated with a specific excess sludge production of 0.4 kg dry matter per kg of COD eliminated. Year 2012 before operation of the AOP is taken as 100 %.

Following tertiary sludge quantity before and after AOP operation is calculated:

- Tertiary sludge DAF 2012 (12 months): 18,901 m^3/a, approx. 662 t/a dry matter (approx. 207 operation days per year)
- Tertiary sludge 2013/2014 (12 months): 3,548 m^3/a, approx.124 t/a dry matter (approx. 33 DAF operation days per year)
- Biological excess sludge biofiltration AOP 2013/2014 approx. 39 t per year (biofilter operation 365 days per year)

The tertiary total DAF sludge based on the data 2012 is reduced by approx. 81 % after operation of the AOP. The (calculated) part of biological excess sludge is below 10 %.

The tertiary sludge reduction results in the following cross-media calculations:

- The tertiary mainly inorganic sludge is reduced by approx. 538 tons per year as dry matter
- The number of DAF operation days 2013/2014 is reduced by 174 days compared to 2012
- Based on an average daily flow 2013/2014 of 11,119 m^3/d and 174 days, 1,935,000 m^3 need not to be treated by DAF
- With an average aluminum dosage of 60 mg/l (equivalent to 661 mg/l $Al_2(SO_4)_3$ x $14H_2O$ as dry substance or 320 mg/l as sulphate) the salt input by sulfate is reduced by 620 t/a
- Assuming that 1 mg/l aluminum (Al^{3+}) is dissolved in the effluent, the input of approx. 1,94 t of Al^{3+} is avoided
- Neutralization chemicals are not considered but might be required in addition if surplus and extended alum dosing is required

The AOP and DAF operation is not yet optimized.

A central optimization measure is the implementation of a load depending COD elimination in the AOP by automated ozone control with use of the online TOC signals for a continuously adjustment of the ozone production (see chapter 8).

7.2 Economic analyses of AOP in comparison to existing DAF

The determination of the main operational cost positions of the conventional DAF system for tertiary treatment and the implemented new AOP system are shown in Table 27.

Table 27: Comparison of main operation cost positions DAF and AOP

Comparison main operation cost AOP versus DAF tertiary effluent treatment, MD Papier GmbH, Plattling		
	AOP	
(calculated on average design data)	part of total operation costs	specific operation costs
	%	ct/m³
Electrical energy ozone generation+ozone injector/diffusor AOP	35%	2.6
Electrical energy biofiltration AOP	5%	0.4
LOX AOP	55%	4.0
Polymer sludge dewatering AOP	2%	0.1
Sludge utilization AOP	4%	0.3
operation costs total AOP	100%	**7.4**
	DAF	
	part of total operation costs	specific operation costs
	%	ct/m³
Electrical energy DAF	8%	0.7
Flocculant and polymer DAF+ polymer sludge dewatering	62%	5.2
Sludge utilization DAF	29%	2.5
operation costs total DAF	100%	**8.4**
	%	ct/m³
Operation cost reduction AOP versus DAF	**-12.2%**	-1.02

The calculation of the operation costs bases on a tertiary COD elimination under average conditions as given in Table 1

The specific energy consumption for the ozone generation is 7.75 kWh/kg of ozone. The injection / diffusor system, biofiltration and off gas compressor require approx. 3,435 kWh/h as electrical energy. The off gas compressor is used continuously for oxygen supply of the high load stage and is included in the power requirement.

The operation costs for sludge utilisation of the DAF sludge, which is further utilized for composting after mixed dewatering with the total biological excess sludge, depend strongly on the actual market prices. Quite low costs for composting are actually achieved and are taken for calculation. An increase of costs of 30 – 50 % or higher was observed in the past years.

The effective yearly operation costs depend on the effective ozone requirement and will be determined after implementation of the required optimization measures as described in chapter 8.1.

The distribution of the cost position AOP and DAF is illustrated in **Figure 47 - Figure 49**.

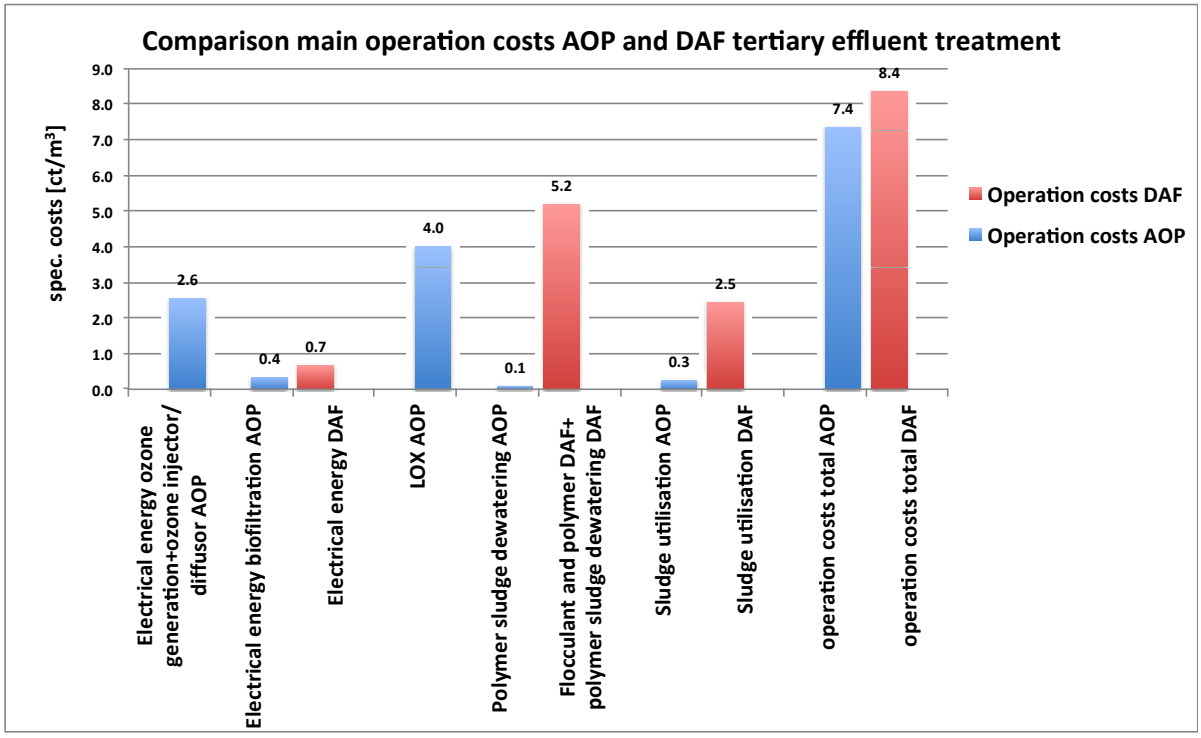

Figure 47: Distribution of main operation costs AOP and DAF in relative costs per kg COD elim

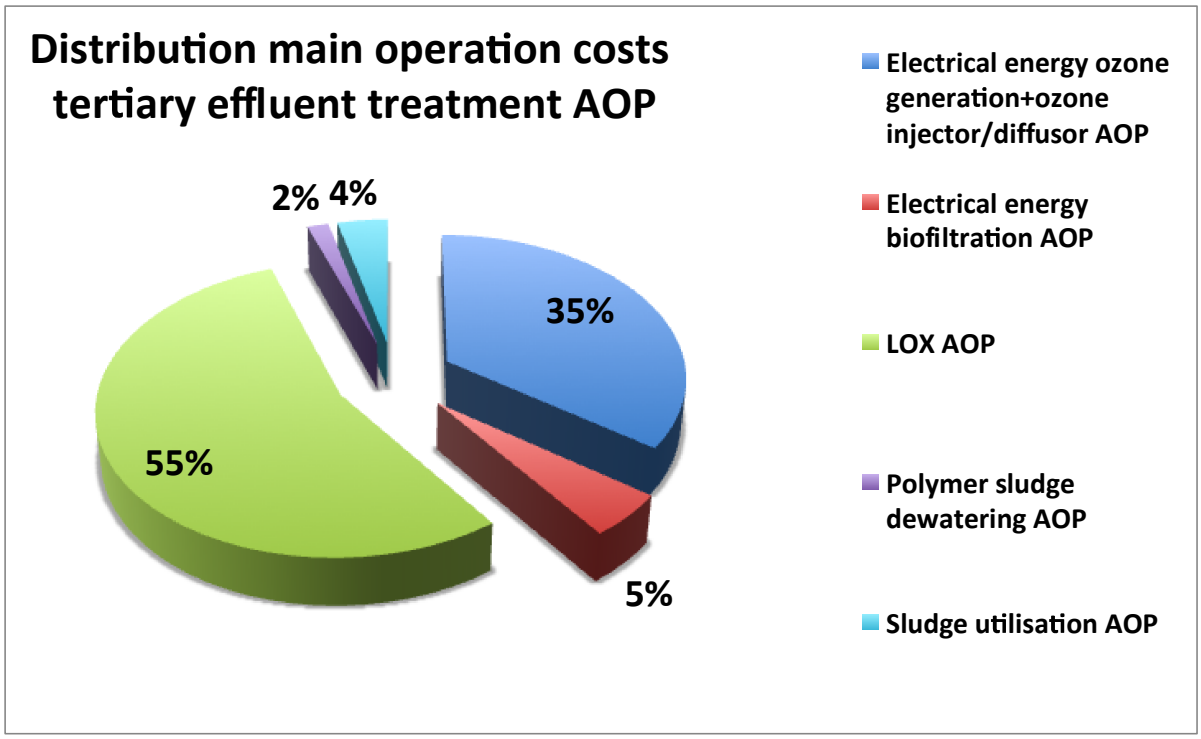

Figure 48: Distribution main operation costs AOP in %

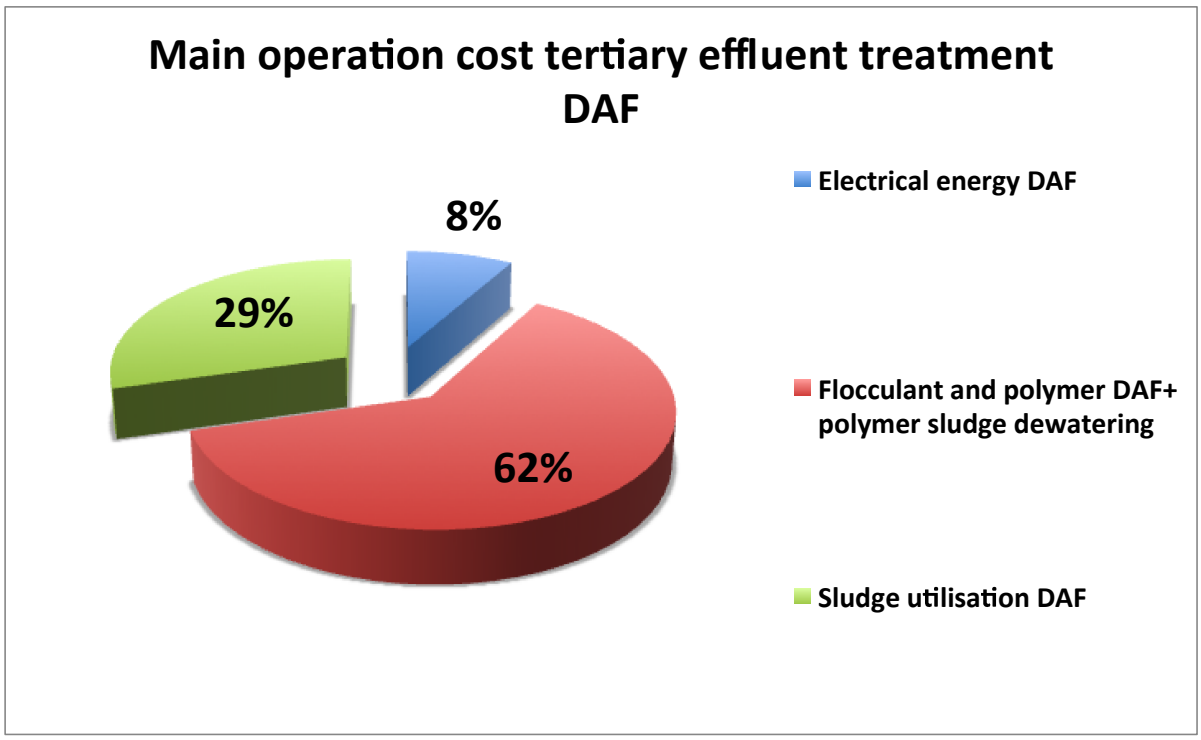

Figure 49: Distribution main operation costs DAF in %

7.3 Cross-media evaluations AOP, energy recovery cooling

The dissipation of the released heat of reaction is effected by a heat exchanger (see chapter 3.6.6). Freshwater produced on site as process water for the papermill is used as cooling water and is tied in after the heat exchanger to the process water supply pipe to the papermill. The required cooling water capacity amounts to approx. 120 m^3/h at a temperature of max. 22 ℃ (delta T is approx. 5 ℃).

The energy recovery for cooling of ozone generator with freshwater which is used as process water and which needs to be less heated amounts to approx. 700 kWh/h as thermal energy when ozone up to the capacity of 50 kg/h is generated.

7.4 Cross-media evaluations AOP, energy recovery from LOX evaporation

LOX as carrier gas for ozone is evaporated in a special LOX water bath vaporiser system.

Up to 500 kg/h of LOX have to be evaporated when 50 kg/h of ozone are generated at 10 wt.-% need to be evaporated. The required cooling water capacity amounts to approx. 30 m^3/h at a temperature of max. 22 ℃ (delta T is appro x. 2 ℃).

The LOX water bath vaporiser is directly connected with a closed cooling water circuit to the ozone generator. The cooling energy for the LOX evaporation is used for cooling the ozone generator (See chapter 3.6.7).

The energy recovery with LOX evaporation in an effective water bath evaporator amounts to approx. 60 kWh/h of thermal energy when ozone up to the capacity of 50 kg/h is generated.

8 Recommendations

8.1 Operation experiences, further optimization requirements

Automatic back flushing filter

The injector / diffusor system of the ozone reactors and the filter floor nozzles in the biofilters are protected by an automatic back flushing filter for separation of coarse solids. Plastics from the waste paper preparation and broken bits of carrier from moving bed biofilm reactor led more often than expected to a blockage of the filter. The system then has to be cleaned manually and the AOP needs to be bypassed.

Additional measures for removal of coarse solids are therefore planned in waste paper preparation directly and in the outlet of the secondary clarifiers for protection of the AOP systems. Modified sieves in the automatic backwash filter have to be tested as well.

Biofilters

The regular aerated surface of the biofilters as shown in Figure 16 changed after several months of operation into an aeration of only certain areas in the filter. The risk is a disturbed air and oxygen supply, which can lead to partial blocking of the filter and building of channels. As a consequence the cubically filtration is insufficient and the biodegradation efficiency decreases. The overall COD removal efficiency of the AOP is then not optimal.

The backwashing steps of the filters have to be intensified. In addition, the filter floor and the filter floor nozzles have to be controlled. If nozzles are blocked the filter has to be emptied and nozzles have to be replaced.

Ozone generation control

The complete automated ozone generation, using the TOC-online analyzer signals, is not fully applied yet. The future target is a complete COD load depending process control for an effective control of the ozone production and avoidance of an ozone overdosing (which results in COD concentrations << 290 mg/l). This can be realized by the calculation of the COD-

load to be eliminated by a constant or ongoing determination of the COD/TOC-ratio using the TOC online signals.

However, more operation experience is required in order to ensure a safe process control philosophy but also to avoid a non-adjusted production of ozone with too high COD removal rates.

Optimization of the ozone distribution between ozone reactor one and two

For the time being the produced ozone is distributed by 50 % into each ozone reactor. The dependency on a modified distribution concept could not yet be studied under normal operation conditions on a long-time basis.

The large-scale test as described in chapter 4.2.1 indicates that a high optimization potential can be achieved if an adopted ozone distribution is applied.

Far more time is needed to get enough data during production days when ozonation is effectively needed.

The optimization of the AOP operation is not yet finalized. However, a distinctly further optimization potential can be expected by applying an adopted ozone control philosophy according to the points as mentioned above.

Both the absolute quantity of ozone and the specific ozone consumption below 0.6 kg of ozone per kg of COD eliminated is expected to be achieved by a successive implementation of these measures. The overall operation costs of the AOP (energy and LOX) will be further reduced as well.

8.2 Model character and further process implementations in other sectors

The applied AOP process in the type of ozonation for chemical oxidation with subsequent treatment in tertiary biofilters for biochemical oxidation has achieved high reputation in one Central European papermill [Kaindl (2006)] with good and stable results.

The optimized AOP process at MD Papier GmbH, Plattling is a consequent further development step towards an improved and energy efficient ozone production by

- Depressurised 2-stage ozone reactor with an upflow bubble column at high efficient counter current
- Extended retention time even for chemical reaction with slow kinetics

- Predominant reaction principle as an intensive „gas to liquid interface“ reaction
- Guided water flow to avoid short cut circuits
- Individual ozone distribution of approx. 0 – 70 % into each reactor

This optimized ozone application can be utilized when a far-reaching elimination of soluble persistent organic compounds to a completely biodegraded effluent has to be applied in environmentally sensitive areas.

The additional simultaneously far reaching elimination of disturbing substances and micropollutants:

- AOX, chelating agents (EDTA and DTPA, for instance), color
- Micro pollutants (Bisphenol A, PAK, PFC (PFOS, PFOA)

  and
- Endocrine disruptors

enables the implementation of the AOP in other industrial sectors such as

- Chemical and pharmaceutical industry
- Textile industry

and in the

- Municipal wastewater treatment for the removal of anthropogenic micro pollutants, which will be an enormous challenge in the future as well.

9 Conclusions

Altogether, the objectives set in the large-scale application of optimized AOP, by applying a further developed innovative ozonation reactor concept, in combination with efficient working biofilters and an overall improved operation, was more than achieved:

- Ensuring an almost entire ozone utilization under atmospheric conditions at relatively high ozone rates has been successfully implemented (without the possibility of conducting pilot tests due to time constraints).

- The cross-media evaluations for the specific electrical energy consumption per kg of COD eliminated provides an improvement of approx. 45 % and documents the enhanced energy efficiency of the optimized AOP concept.

- Although the hydraulic capacity of the AOP is up to 55 % of the total flow, the number of operation days of the existing DAF could be substantially decreased by more than 80 %, even less DAF operating days are expected in the future.

- The tertiary inorganic sludge amount is accordingly reduced by over 80 % and the environmental disadvantages are substantially avoided (further optimizations are in preparation, see further comments below).

- The main objective in the future is to significantly protect receiving water in the river Isar in a sensitive FFH conservation area beyond the minimum statutory requirements and sustainably develop the reduction of the final organic residue discharge below 3.0 kg/t COD with an environmentally friendly process.

- An efficient reduction beyond AOX, chelating agents, and the priority substances associated micro pollutants such as BPA, PAH and in significantly reducing the endocrine disrupters of wastewater shows the potential for a sustained improvement in effluent quality for the application of AOP

The target to achieve a stable range between 0.4 - 0.6 kg ozone per kg of COD could not yet be reached (0.8 kg ozone per kg of COD eliminated is achieved on average).

To achieve this objective, it is necessary to optimize the partial oxidation, while increasing the concentration of biodegradable organic compounds (increase of BOD/COD-ratio) and biodegradation in the biofiltration instead of applying a pure chemical oxidation.

The optimization potential during operation, which could not yet be investigated, is the variable distribution of ozone per reactor (so far it is split evenly), the operation of only one reactor depending on the load to be eliminated, as well as the optimization of the hydraulic retention time (reducing or increasing the amount of wastewater within the possible operating range).

A general optimization potential is expected by applying a complete COD load depending ozone generation control using the TOC online signals inlet and outlet and a validated COD/TOC-ratio basis for an automated load depending process control to avoid a far reaching COD elimination below the required optimum.

With the implementation of a load dependent on the TOC-online measurements automated control, the optimum operating range can generally be monitored and the operating costs are further reduced.

The operational experiences gained since this rather short operation period already show, that choosing a flexible process with adjustable operation conditions is beneficial and necessary to ensure that the practical operation will allow the required adjustments for effective elimination of solutes as a function of the ultimate complex reaction kinetics.

Although micro pollutants and endocrine disrupters are found near or below the detection limit after the WWTP at MD Papier GmbH, their elimination is not subject to environmental regulations. The high elimination efficiency for many of these substances by applying AOP will help to improve the water quality of the receiving waters even in the future.

The implementation of a sustainable water management is in accordance with the policy of high environmental protection objectives within the UPM Group in general and on site at MD Papier GmbH Plattling.

Funding programs such as the BMUB Environment Innovation Program of the Federal Environmental Ministry (BMUB) enable the large-scale implementation of such innovative projects.

Upgrading industrial plants and the continuous improvement in dialogue with regional and national expert authorities provide valuable information that can be used for municipal wastewater and for wastewater from other industrial sectors and thus contribute to a further improvement of the environmental performance of large scale installations.

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11 Annexes

- Annex 1: Annex 1, Table 1 – Annex 1, Table 5: statistical operation data evaluation AOP August 2013 - October 2014

- Annex 2: Report Endocrine Disrupting Substances

Annex 1, Table 1: statistical data evaluation August 2013 - October 2014

date	AOP inflow (inflow ozone reactor 1)								AOP inflow ozone reactor 1 (8 a.m.)					
	inflow from LWC 1 Q m³/d -	inflow from LWC 2 m³/d -	inflow from SC m³/d -	Inflow AOP (IDM calculated) m³/d -	peak flow pass LWC to DAF SC m³/d -	water biofiltration (AOP) zu wwtp SC m³/d -	pass LWC to main outlet channel m³/d -	Clearwater outlet AOP total m³/d -	SS mg/l -	BOD_5 mg/l filtered	COD from SC mg/l filtered	TOC from SC mg/l (reading)	COD from LWC mg/l filtered	TOC from LWC mg/l (reading)
01/08/13	5,045.30	5,807.40	11,322.9	11,322.9	0.0	466.9	10,852.7	10,004.2	7.05					
23/10/14	5,295.40	4,789.80	2.40	9,821.30	263.90	635.40	0.00	9,077.30					247.00	99.00
31/12/14														
Statistic "ARADAT" SC und LWC AOP 01.08.2013 - 31.12.2014														
md	5,141.80	4,326.70	1,017.80	10,006.80	3.80	737.40	1,696.30	8,922.30	10.99	12.00	265.00	91.50	244.00	94.00
mv	5,079.32	4,281.16	4,323.60	9,809.45	66.09	736.06	3,805.98	8,662.20	10.72	13.55	257.86	88.47	251.79	95.22
s	775.04	742.69	5,070.01	2,086.66	185.19	287.50	4,142.97	1,767.29	2.76	7.70	64.51	26.69	61.60	20.51
v %	15.26	17.35	117.26	21.27	280.20	39.06	108.85	20.40	25.77	56.82	25.02	30.17	24.46	21.54
min	1,450.60	1,416.30	0.40	0.00	0.00	0.00	0.00	10.90	5.00	2.00	68.00	12.00	117.00	41.00
max	6,765.30	6,526.40	12,221.30	12,221.30	2,365.10	1,958.30	12,226.50	11,100.60	16.00	44.00	434.00	130.00	542.00	150.00
mv+s	5,854.37	5,023.85	9,393.61	11,896.10	251.28	1,023.56	7,948.95	10,429.49	13.49	21.25	322.37	115.17	313.38	115.73
80-percentile	5,702.60	4,877.00	11,322.90	11,659.20	75.40	895.10	8,621.20	10,027.30	13.00	17.00	304.00	111.00	296.40	111.83
85-percentile	5,859.80	5,034.65	11,821.10	11,852.90	107.50	933.75	9,253.50	10,105.50	13.04	20.05	316.30	114.50	302.55	116.00
mv+2s	6,629.41	5,766.54	14,463.63	13,982.76	436.47	1,311.06	12,091.92	12,196.78	16.25	28.95	386.88	141.86	374.98	136.24
95-percentile	6,160.95	5,364.60	12,066.00	12,066.00	326.75	1,308.70	10,692.60	10,450.35	14.64	31.40	336.00	123.00	349.70	131.05
mv-s	4,304.28	3,538.46	-746.42	7,722.79	-119.10	448.57	-336.99	6,894.91	7.96	5.85	193.34	61.78	190.19	74.71
mv-2s	3,529.24	2,795.77	-5,816.43	5,636.13	-304.29	161.07	-4,479.96	5,127.62	5.20	-1.85	128.83	35.09	128.59	54.20
sum	2,189,189	1,845,178	1,863,471	4,227,871	28,486	317,244	1,640,377	3,733,407	386.08	1,545.00	23,207.00	5,839.18	41,293.00	13,140.17
n	431.00	431.00	431.00	431.00	431.00	431.00	431.00	431.00	36.00	114.00	90.00	66.00	164.00	138.00

Annex 1, Table 2: statistical data evaluation August 2013 - October 2014 (continuation)

date	AOP inflow ozone reactor 1 (8 a.m.)							AOP outflow ozone reactor 2 (grab sample +1h)						
	NH_4-N	NO_3-N	inorg.N	P_{tot}.	t max.	TOC to AOP from LWC average	TOC to AOP from SC average	BOD_5	COD	NH_4-N	NO_3-N	inorg.N	P_{tot}.	SS
	mg/l filtered	mg/l filtered	mg/l filtered	mg/l filtered	°C -	mg/l online	mg/l online	mg/l filtered	mg/l filtered	mg/l filtered	mg/l filtered	mg/l filtered	mg/l filtered	mg/l -
01/08/13					32.76	87.80	92.80							
23/10/14	0.21	1.75	1.96	0.23	23.48	94.42	64.49		201.00	0.18	1.75	1.93	0.24	31.00
31/12/14														
Statistic "ARADAT" SC und LWC AOP 01.08.2013 - 31.12.2014														
md	0.22	2.08	2.53	0.30	28.10	91.63	87.08	13.00	240.00	0.29	2.12	2.66	0.34	7.00
mv	0.92	2.21	3.11	0.43	27.77	90.24	85.65	16.44	240.66	1.01	2.30	3.30	0.47	17.68
s	1.66	0.73	1.76	0.34	4.04	24.60	28.00	10.69	54.82	1.66	0.90	1.88	0.35	35.73
v %	180.44	32.90	56.70	78.71	14.55	27.26	32.69	65.00	22.78	164.33	39.35	56.89	75.25	202.08
min	0.02	0.91	1.06	0.03	12.88	0.00	4.07	2.00	70.00	0.05	0.96	1.17	0.05	0.01
max	10.50	6.63	12.90	2.14	55.17	149.90	159.60	47.00	487.00	10.20	8.94	12.60	2.13	300.00
mv+s	2.58	2.94	4.87	0.76	31.81	114.84	113.65	27.13	295.48	2.66	3.20	5.18	0.82	53.41
80-percentile	1.19	2.52	3.70	0.70	31.11	108.90	110.08	24.60	284.00	1.25	2.56	3.96	0.75	19.60
85-percentile	1.83	2.65	4.22	0.82	31.64	114.57	114.01	28.90	293.00	2.00	2.71	4.73	0.87	26.20
mv+2s	4.24	3.67	6.63	1.10	35.85	139.45	141.66	37.82	350.30	4.32	4.11	7.05	1.17	89.14
95-percentile	4.92	3.55	6.85	1.04	32.84	126.73	127.02	40.60	318.35	4.81	3.69	7.29	1.12	90.00
mv-s	-0.74	1.48	1.35	0.09	23.73	65.64	57.65	5.75	185.84	-0.65	1.39	1.42	0.12	-18.05
mv-2s	-2.40	0.76	-0.42	-0.25	19.69	41.03	29.65	-4.93	131.02	-2.30	0.49	-0.45	-0.24	-53.78
sum	233.69	561.75	748.70	108.27	11,939.97	39,163.82	37,173.32	1,891.00	60,646.00	253.80	579.36	821.61	117.31	4,119.56
n	254.00	254.00	241.00	253.00	430.00	434.00	434.00	115.00	252.00	252.00	252.00	249.00	251.00	233.00

Annex 1, Table 3: statistical data evaluation August 2013 - Oktober 2014 (continuation)

Datum	AOP outflow biofilter (total outflow) (grab sample +2h)												
	pH	BOD_5	COD	TOC	NH_4-N	NO_3-N	NO_2-N	inorg.N	P_{tot}.	AOX	TOC average	O_3 wt. - %	O_3 kg/d
	-	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l		
	-	filtriert	filtriert	(abgelesen)	filtriert	filtriert	filtriert	filtriert	filtriert	-	online	O_3 > 9.0 wt. %	
01/08/13											77.50		
23/10/14	8.07		201.00		0.06	1.66		1.72	0.24		86.41		
31/12/14													
Statistic "ARADAT" SC und LWC AOP 01.08.2013 - 31.12.2014													
md	8.04	10.00	210.00	82.00	0.12	2.22	#ZAHL!	2.39	0.35	#ZAHL!	80.24	9.93	894.30
mv	8.03	11.43	214.51	81.01	0.39	2.61	#DIV/0!	2.99	0.42	#DIV/0!	80.97	9.77	870.23
s	0.18	7.08	45.81	17.86	0.86	1.27	#DIV/0!	1.69	0.26	#DIV/0!	21.34	0.30	248.03
v %	2.28	61.94	21.35	22.05	224.59	48.77	#DIV/0!	56.52	60.91	#DIV/0!	26.36	3.09	28.50
min	7.38	2.00	67.00	0.10	0.02	0.30	0.00	1.06	0.09	0.00	-2.93	9.07	384.10
max	8.80	44.00	434.00	125.00	6.32	9.19	0.00	12.26	1.42	0.00	193.85	10.04	1,273.80
mv+s	8.22	18.52	260.32	98.87	1.25	3.88	#DIV/0!	4.68	0.68	#DIV/0!	102.31	10.07	1,118.25
80-percentile	8.20	15.20	248.00	96.00	0.30	3.07	#ZAHL!	3.60	0.65	#ZAHL!	95.54	10.00	1,114.58
85-percentile	8.20	16.00	259.50	98.00	0.52	3.38	#ZAHL!	4.13	0.71	#ZAHL!	99.50	10.00	1,169.65
mv+2s	8.40	25.60	306.13	116.73	2.11	5.15	#DIV/0!	6.37	0.93	#DIV/0!	123.66	10.38	1,366.28
95-percentile	8.30	23.30	288.75	107.55	1.67	5.44	#ZAHL!	6.61	0.92	#ZAHL!	109.53	10.01	1,229.25
mv-s	7.85	4.35	168.71	63.15	-0.48	1.33	#DIV/0!	1.30	0.16	#DIV/0!	59.63	9.47	622.20
mv-2s	7.67	-2.73	122.90	45.29	-1.34	0.06	#DIV/0!	-0.39	-0.09	#DIV/0!	38.29	9.17	374.18
sum	1,928.34	1,315.00	52,770.00	15,391.48	94.72	640.89	0.00	729.57	102.53	0.00	35,142.52	674.26	59,175.50
n	240.00	115.00	246.00	190.00	246.00	246.00	0.00	244.00	244.00	0.00	434.00	69.00	68.00

Annex 1, Table 4: statistical data evaluation August 2013 - Oktober 2014 (continuation)

Datum	Ozone generation					Inflow ozone reactor 1			Outflow ozone reactor 2					
	$O_{3\text{-offgas}}$ wt. - %	O_3 kg/h	O_3 kWh/d O_3 > 9.0 wt. %	O_3 kWh/h	O_3 kWh/kg	$B_{d,\ COD\ in}$ kg/d -	BOD/COD $_{in}$ -	CSB/TOC $_{in}$ -	$B_{d,\ COD\ out\ O3}$ kg/d -	BSB/CSB out O3 -	$B_{d,\ COD\ elim\ O3}$ kg/d	all data η COD out O3 %	**ozonation only** η CSB out O3 %	$B_{d,\ COD\ elim\ BF}$ kg/d
01/08/13														
23/10/14						2,141.51		2.49	1,952.25		446.78	18.62		0.00
31/12/14														
Statistic "ARADAT" SC und LWC AOP 01.08.2013 - 31.12.2014														
md	99.97	37.26	6,835.54	284.81	7.64	2,471.93	0.05	2.61	2,336.39	0.06	39.54	1.88	8.88	258.73
mv	99.86	36.26	6,795.07	283.13	7.75	2,463.46	0.05	2.72	2,290.46	0.07	122.71	4.48	8.36	277.66
s	0.24	10.33	2,752.63	114.69	2.09	814.97	0.03	0.50	660.54	0.04	236.11	8.95	10.12	217.06
v %	0.24	28.50	40.51	40.51	27.04	33.08	52.07	18.40	28.84	61.22	192.42	199.59	121.09	78.18
min	98.63	16.00	0.58	0.02	0.00	0.00	0.01	1.77	2.26	0.01	-592.44	-25.21	-25.21	-306.89
max	100.00	53.08	10,944.17	456.01	12.25	4,926.89	0.18	6.06	4,641.06	0.20	998.81	39.86	39.86	1,268.28
mv+s	100.10	46.59	9,547.70	397.82	9.84	3,278.44	0.08	3.22	2,951.00	0.11	358.82	13.43	18.47	494.72
80-percentile	100.00	46.44	9,429.59	392.90	9.07	3,087.63	0.07	2.88	2,856.04	0.10	294.83	11.57	17.85	466.89
85-percentile	100.00	48.74	10,052.43	418.85	9.60	3,231.51	0.08	3.03	2,979.77	0.11	421.95	15.12	18.92	488.87
mv+2s	100.34	56.93	12,300.33	512.51	11.94	4,093.41	0.11	3.72	3,611.55	0.15	594.92	22.38	28.59	711.78
95-percentile	100.00	51.22	10,647.76	443.66	10.85	3,702.38	0.11	3.53	3,326.44	0.16	601.63	22.43	23.20	624.81
mv-s	99.61	25.93	4,042.44	168.43	5.65	1,648.49	0.03	2.22	1,629.92	0.03	-113.40	-4.47	-1.76	60.59
mv-2s	99.37	15.59	1,289.81	53.74	3.56	833.52	0.00	1.72	969.37	-0.02	-349.51	-13.41	-11.88	-156.47
sum	6,690.43	2,465.65	380,523.8	15,855.16	433.78	775,991.22	6.23	535.98	565,743.39	7.30	30,308.46	1,062.56	868.92	60,806.82
n	67.00	68.00	56.00	56.00	56.00	315.00	114.00	197.00	247.00	106.00	247.00	237.00	104.00	219.00

Annex 1, Table 5: statistical data evaluation August 2013 - October 2014 (continuation)

date	Outflow biofilter stage (BF)				total outflow AOP (outflow BF)										
	η COD BF	η BOD BF	data without ozonation	data with ozonation only η CSB	$B_{d,\ COD\ out}$	BSB/CSB out	COD/TOC out	$B_{d,\ COD\ elim}$	O_3 / COD elim	all data η COD total AOP	data with ozonation only η CSB total AOP	η TOC total AOP	COD inflow AOP (LWCand SC)	O_3 / COD total inflow
	%	%	%	%	kg/d	-	-	kg/d	kg/kg	%	%	%	mg/l	kg/kg
					-			-	-				filtered	-
								O_3 > 9,0 wt.-%						
01/08/13														
23/10/14					1,952.25					18.62			247.00	
31/12/14														
Statistic "ARADAT" SC und LWC AOP 01.08.2013 - 31.12.2014														
md	11.11	23.30	9.66	13.25	2,005.23	0.05	2.59	959.23	0.84	13.62	20.47	13.11	250.00	0.31
mv	11.40	4.53	9.59	13.65	2,046.76	0.05	2.62	966.14	0.90	15.70	20.79	10.95	253.94	0.32
s	8.58	88.69	7.98	9.01	596.58	0.03	0.34	248.43	0.22	10.13	11.23	23.81	62.59	0.07
v %	75.27	1,956.95	83.17	66.01	29.15	55.88	12.80	25.71	24.82	64.51	53.99	217.51	24.65	22.11
min	-22.83	-600.00	-22.83	-14.53	0.00	0.01	1.32	583.87	0.52	-12.21	-6.98	-128.57	68.00	0.18
max	51.31	70.21	32.26	51.31	3,829.62	0.18	4.00	1,524.78	1.30	46.31	46.31	99.91	542.00	0.46
mv+s	19.98	93.22	17.56	22.66	2,643.34	0.08	2.96	1,214.57	1.13	25.83	32.02	34.76	316.52	0.39
80-percentile	18.59	48.41	14.95	20.36	2,495.45	0.07	2.83	1,085.70	1.10	22.71	31.13	22.11	298.80	0.36
85-percentile	19.98	50.00	17.48	21.34	2,698.04	0.07	2.91	1,182.71	1.17	27.57	32.18	27.42	312.05	0.42
mv+2s	28.56	181.91	25.54	31.67	3,239.92	0.11	3.29	1,463.00	1.35	35.96	43.25	58.56	379.11	0.46
95-percentile	23.58	57.43	21.70	25.88	2,973.91	0.12	3.06	1,441.42	1.29	34.90	40.87	36.63	348.70	0.44
mv-s	2.82	-84.16	1.61	4.64	1,450.18	0.02	2.29	717.70	0.68	5.57	9.57	-12.86	191.35	0.25
mv-2s	-5.76	-172.84	-6.36	-4.37	853.60	-0.01	1.95	469.27	0.46	-4.56	-1.66	-36.67	128.77	0.18
sum	2,473.60	271.92	1,102.68	1,310.57	501,455.59	6.21	419.33	29,950.21	27.14	3,768.56	2,162.64	1,762.33	64,500.00	9.83
n	217.00	60.00	115.00	96.00	245.00	115.00	160.00	31.00	30.00	240.00	104.00	161.00	254.00	31.00

Annex 2: Report Endocrine Disrupting Substances

Ergebnisse des Hefetests, R-YEA, auf östrogene Wirkungen der Abwasserproben:

Probe „Ablauf Vorklärung ARA LWC“:

	NK	G192	G96	G48	G24	G12	G6	G3	G 1,5
ß-gal/zelld.	**997**	**771**	**769**	**639**	**480**	**492**	**470**	**449**	**548**
+/-	116	64,7	79,2	73,7	24,4	37,9	25,9	79,6	61,5
+/- in %	11,7	8,4	10,3	11,5	5,1	7,7	5,5	17,7	11,2
Induktionsrate	**1,0**	**0,8**	**0,8**	**0,6**	**0,5**	**0,5**	**0,5**	**0,5**	**0,5**
%-Zellen	**100,0**	**94,7**	**95,4**	**99,9**	**103,2**	**107,1**	**107,7**	**108,2**	**102,8**
OD (595 nm)	0,686	0,649	0,654	0,685	0,708	0,734	0,739	0,742	0,705
+/-	0,023	0,030	0,039	0,021	0,034	0,012	0,021	0,033	0,035
OD (420 nm)	0,691	0,519	0,520	0,462	0,371	0,392	0,379	0,364	0,413

NK: Negativkontrolle G: Verdünnungsstufe nach DIN (G 1,5 = 1:1,5); OD: Optische Dichte
Die Zellzahlbestimmung erfolgt durch die Bestimmung der Optischen Dichte bei 595 nm (OD 595).
Die Aktivität der ß-Galaktosidase wird über die Gelbfärbung bei 420 nm bestimmt.

Die Probe wies ein hemmendes Potential auf. Dabei handelt es sich wahrscheinlich um eine Hemmung der ß-Galaktosidase, theoretisch ist aber auch eine antiöstrogene Wirkung möglich. Ersteres wird beim nächsten Hefetest überprüft. **Die Ermittlung einer östrogenen Wirkung war somit nicht möglich.**

Probe „Ablauf Nachklärung ARA LWC“:

	NK	G192	G96	G48	G24	G12	G6	G3	G 1,5
ß-gal/zelld.	**1232**	**1160**	**1179**	**1294**	**1681**	**1812**	**2118**	**2925**	**4293**
+/-	104	111,0	107,5	119,3	100,2	106,1	103,7	269,2	567,5
+/- in %	8,4	9,6	9,1	9,2	6,0	5,9	4,9	9,2	13,2
Induktions-rate	**1,0**	**0,9**	**1,0**	**1,1**	**1,4**	**1,5**	**1,7**	**2,4**	**3,5**
%-Zellen	**100,0**	**99,0**	**99,9**	**97,9**	**102,8**	**105,2**	**105,3**	**112,5**	**104,9**
OD (595 nm)	0,648	0,641	0,647	0,634	0,666	0,681	0,682	0,729	0,679

+/-	0,033	0,022	0,047	0,044	0,023	0,031	0,024	0,048	0,024
OD (420 nm)	0,859	0,808	0,825	0,877	1,162	1,270	1,468	2,116	2,846
+/-	0,062	0,054	0,046	0,041	0,041	0,027	0,043	0,139	0,338

NK: Negativkontrolle G: Verdünnungsstufe nach DIN (G 1,5 = 1:1,5); OD: Optische Dichte
Die Zellzahlbestimmung erfolgt durch die Bestimmung der Optischen Dichte bei 595 nm (OD 595).
Die Aktivität der ß-Galaktosidase wird über die Gelbfärbung bei 420 nm bestimmt.

Die Probe wies ein deutliches östrogenes Potenzial auf. Bei einer Verdünnung von 1:12 war noch eine östrogene Wirkung messbar.

Probe „Ablauf Ozonreaktoren ARA LWC“:

	NK	**G192**	**G96**	**G48**	**G24**	**G12**	**G6**	**G3**	**G 1,5**
ß-gal/zelld.	**1318**	**1430**	**1125**	**1232**	**1414**	**1326**	**1424**	**1700**	**1809**
+/-	205,73	217,79	153,63	124,46	209,03	226,65	108,16	197,73	153,81
+/- in %	15,6	15,2	13,7	10,1	14,8	17,1	7,6	11,6	8,5
Induktions-rate	**1,0**	**1,1**	**0,9**	**0,9**	**1,1**	**1,0**	**1,1**	**1,3**	**1,4**
%-Zellen	**100,0**	**101,8**	**100,2**	**104,5**	**102,3**	**103,2**	**106,7**	**111,4**	**115,6**
OD (595 nm)	**0,647**	**0,659**	**0,649**	**0,677**	**0,662**	**0,668**	**0,691**	**0,721**	**0,748**
+/-	0,019	0,036	0,028	0,033	0,033	0,042	0,038	0,037	0,030
OD (420 nm)	0,921	1,002	0,805	0,906	0,999	0,951	1,050	1,278	1,405
+/-	0,117	0,102	0,086	0,079	0,103	0,131	0,088	0,124	0,121

NK: Negativkontrolle G: Verdünnungsstufe nach DIN (G 1,5 = 1:1,5); OD: Optische Dichte
Die Zellzahlbestimmung erfolgt durch die Bestimmung der Optischen Dichte bei 595 nm (OD 595).
Die Aktivität der ß-Galaktosidase wird über die Gelbfärbung bei 420 nm bestimmt.

Die Probe zeigt in der höchsten getesteten Konzentration eine Induktionsrate der ß-Galaktosidase mit einem Wert von 1,4. Dieser Wert liegt knapp unter der bislang festgelegten Grenze von 1,5, ist jedoch signifikant positiv. Dass es sich um eine reelle Erhöhung handelt, zeigen die Messwerte der OD 420-Bestimmung mit 0,921 bei der Negativkontrolle und 1,405 bei der G 1,5-Verdünnung.

Probe „Ablauf Biofilter“:

	NK	**G192**	**G96**	**G48**	**G24**	**G12**	**G6**	**G3**	**G 1,5**
ß-gal/zelld.	**1214**	**1302**	**1219**	**1035**	**1000**	**1148**	**1353**	**1425**	**1871**
+/-	154,38	180,23	78,80	143,24	227,94	237,85	251,63	308,64	314,12
+/- in %	12,7	13,8	6,5	13,8	22,8	20,7	18,6	21,7	16,8

Induktionsrate	1,0	1,1	1,0	0,9	0,8	0,9	1,1	1,2	1,5
%-Zellen	**104,6**	**101,4**	**96,3**	**99,1**	**103,1**	**101,8**	**105,1**	**104,9**	**109,7**
OD (595 nm)	0,677	0,656	0,623	0,641	0,667	0,659	0,680	0,679	0,710
+/-	0,020	0,020	0,015	0,011	0,016	0,023	0,023	0,022	0,041
OD (420 nm)	0,893	0,922	0,832	0,743	0,746	0,830	0,992	1,032	1,380
+/-	0,082	0,091	0,032	0,081	0,133	0,137	0,183	0,196	0,235

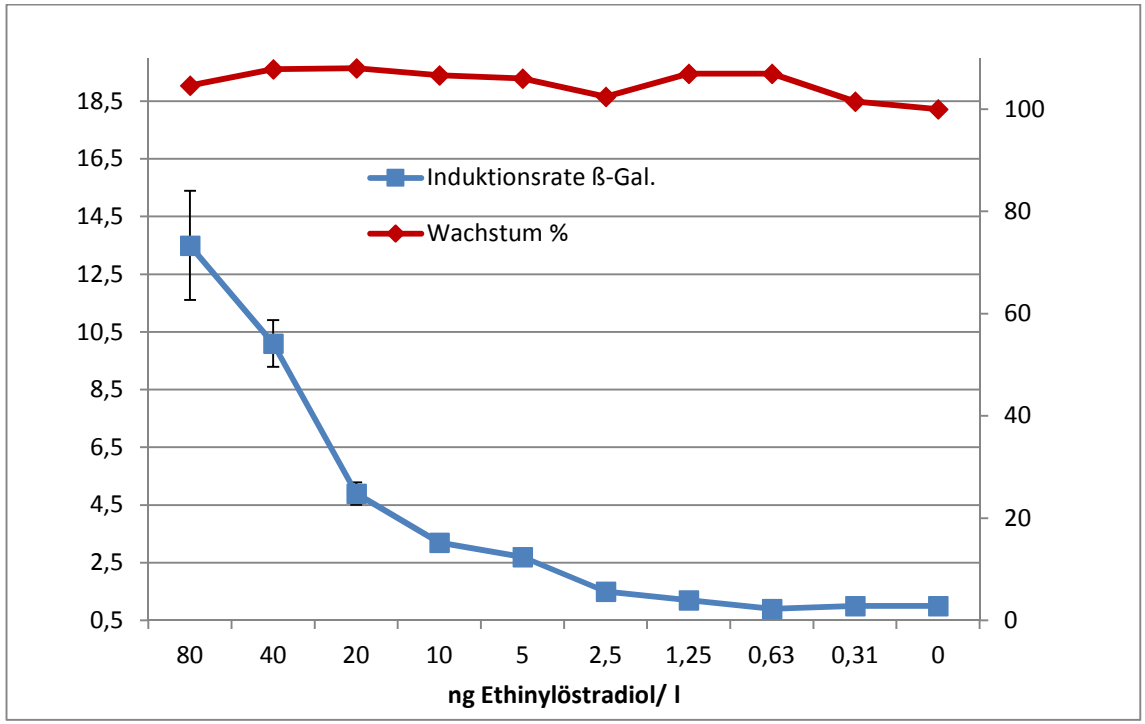
NK: Negativkontrolle G: Verdünnungsstufe nach DIN (G 1,5 = 1:1,5); OD: Optische Dichte
Die Zellzahlbestimmung erfolgt durch die Bestimmung der Optischen Dichte bei 595 nm (OD 595).
Die Aktivität der ß-Galaktosidase wird über die Gelbfärbung bei 420 nm bestimmt.

Die Probe wies in der höchsten getesteten Konzentration ein signifikantes östrogenes Potenzial auf.
Bei allen 4 Proben war keine zytotoxische Wirkung messbar. Die Trübungen der Proben wurden durch die Mitführung von Blindwerten berücksichtigt.

Als Positivkontrolle diente eine Konzentrations-Wirkungs-Kurve mit 17-Ethinylöstradiol (s.u.).

Ethinylöstradiol:

	NK	**0,63 ng/l**	**1,25 ng/l**	**2,5 ng/l**	**5,0 ng /l**	**10,0 ng/l**	**20,0 ng/l**	**40,0 ng/l**	**80,0 ng/l**
ß-gal/zelld.	**258**	**316**	**392**	**531**	**702**	**827**	**1264**	**2615**	**3483**
+/-	41	55,2	33,5	17,0	21,5	68,0	98,6	214,5	494,8
+/- in %	15,8	17,4	8,5	3,2	3,1	8,2	7,8	8,2	14,2
Induktionsrate	**1,0**	**1,2**	**1,5**	**2,1**	**2,7**	**3,2**	**4,9**	**10,1**	**13,5**
%-Zellen	**100,0**	**106,9**	**102,4**	**106,2**	**106,6**	**108,0**	**108,7**	**107,8**	**104,6**
OD (595 nm)	**0,668**	**0,714**	**0,684**	**0,709**	**0,712**	**0,721**	**0,726**	**0,720**	**0,698**
+/-	0,034	0,056	0,030	0,011	0,027	0,020	0,026	0,047	0,031
OD (420 nm)	0,208	0,259	0,299	0,403	0,519	0,611	0,915	1,823	2,336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Induktionsrate ß-Gal.
Wachstum %
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ng Ethinylöstradiol/ l