

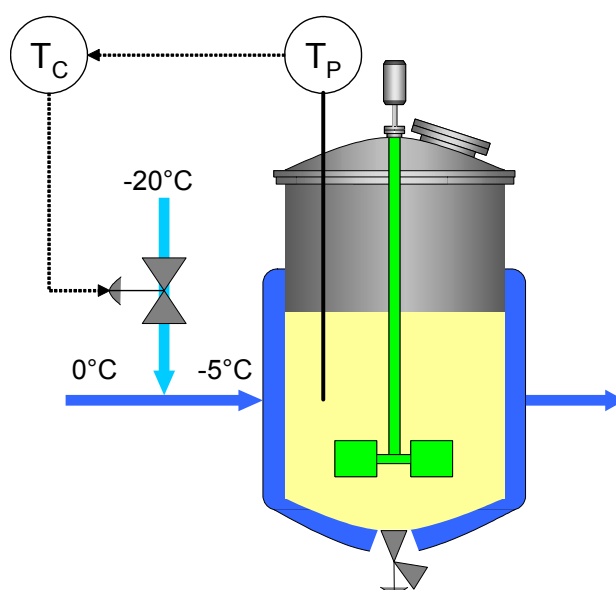


EUROPEAN COMMISSION  
DIRECTORATE-GENERAL JRC  
JOINT RESEARCH CENTRE  
Institute for Prospective Technological Studies

# Integrated Pollution Prevention and Control

## Reference Document on Best Available Techniques for the Manufacture of Organic Fine Chemicals

Dated December 2005





## EXECUTIVE SUMMARY

The BAT (Best Available Techniques) Reference Document (BREF) entitled “Best Available Techniques for the Manufacture of Organic Fine Chemicals” (OFC) reflects an information exchange carried out under Article 16(2) of Council Directive 96/61/EC (IPPC Directive). This executive summary describes the main findings, a summary of the principal BAT conclusions and the associated consumption and emission levels. It should be read in conjunction with the preface, which explains this document’s objectives; how it is intended to be used and legal terms. It can be read and understood as a standalone document but, as a summary, it does not present all the complexities of this full document. It is therefore not intended as a substitute for this full document as a tool in BAT decision making.

This document focuses on the batch manufacture of organic chemicals in multipurpose plants and addresses the manufacture of a wide range of organic chemicals although not all of them are explicitly named in ANNEX 1 of the Directive. The list is not conclusive but includes, e.g. dyes and pigments, plant health products and biocides, pharmaceutical products (chemical and biological processes), organic explosives, organic intermediates, specialised surfactants, flavours, fragrances, pheromones, plasticisers, vitamins, optical brighteners and flame-retardants. No specific threshold was established in drawing a borderline to large volume production. Therefore it is implied that an OFC production site may also include dedicated production lines for “larger” volume products with batch, semi-batch or continuous operation.

### I. The sector and environmental issues

Organic fine chemical manufacturers produce a range of chemical substances, which are typically of a high added-value and produced in low volumes, mainly by batch processes in multipurpose plants. They are sold to companies, mostly other chemical companies, serving an immense range of end-user markets, on either a specification of purity or on their ability to deliver a particular effect. OFC manufacturers range in size from very small (<10 staff) to very large multinationals (>20000 staff), with typical manufacturing sites having between 150 and 250 staff.

The chemistry of fine organic intermediates and products shows an enormous diversity. But in reality, the number of operations/processes used remains reasonably small. These include charging/discharging of reactants and solvents, inertisation, reactions, crystallisations, phase separations, filtrations, distillation, product washing. In many cases cooling, heating, or the application of vacuum or pressure is necessary. The unavoidable waste streams are treated in recovery/abatement systems or disposed of as waste.

The key environmental issues of the OFC sector are emissions of volatile organic compounds, waste waters with potential for high loads of non-degradable organic compounds, relatively large quantities of spent solvents and non-recyclable waste in high ratio. Given the diversity of the sector, the wide range of chemicals produced and the enormous variety of possibly emitted substances, this document does not provide a comprehensive overview of the releases from the OFC sector. No data on consumption of raw materials, etc. were available. However, emission data are presented from a broad range of example plants in the OFC sector.

### II. Techniques to consider in the determination of BAT

The techniques to consider in the determination of BAT are grouped under the headings “Prevention and minimisation of environmental impact” (much related to the process design) and the “Management and treatment of waste streams”. The former includes strategies for the selection of the synthesis route, examples of alternative processes, equipment selection and plant design. The management of waste streams includes techniques for the assessment of waste stream properties and the understanding and monitoring of emissions. Finally, a wide range of recovery/abatement techniques for the treatment of waste gases, the pretreatment of waste water streams and the biological treatment of the total waste water are described.

### **III. Best available techniques**

The summary presented below does not include background statements and cross referencing which is found in the full text. Additionally, the full text contains BAT on environmental management. Where general BAT associated emission levels are given both in terms of concentration and mass flow, that which represents the greater amount in specific cases is intended as the BAT reference.

### **Prevention and minimisation**

#### **Integration of environmental considerations into process development**

BAT is to provide an auditable trail for the integration of environmental, health and safety considerations into process development. BAT is to carry out a structured safety assessment for normal operation and to take into account effects due to deviations of the chemical process and deviations in the operation of the plant. BAT is to establish and implement procedures and technical measures to limit risks from the handling and storage of hazardous substances and to provide sufficient and adequate training for operators who handle hazardous substances. BAT is to design new plants in such a way that emissions are minimised. BAT is to design, build, operate and maintain facilities, where substances (usually liquids) which represent a potential risk of contamination of ground and groundwater are handled, in such a way that spill potential is minimised. Facilities have to be sealed, stable and sufficiently resistant against possible mechanical, thermal or chemical stress. BAT is to enable leakages to be quickly and reliably recognised. BAT is to provide sufficient retention volumes to safely retain spills and leaking substances, fire fighting water and contaminated surface water in order to enable treatment or disposal.

#### **Enclosure of sources and airtightness of equipment**

BAT is to contain and enclose sources and to close any openings in order to minimise uncontrolled emissions. Drying should be carried out by using closed circuits, including condensers for solvent recovery. BAT is to use recirculation of process vapours where purity requirements allow this. To minimise the volume flow, BAT is to close any unnecessary openings in order to prevent air being sucked to the gas collection system via the process equipment. BAT is to ensure the airtightness of process equipment, especially of vessels. BAT is to apply shock inertisation instead of continuous inertisation. Still, continuous inertisation has to be accepted due to safety requirements, e.g. where processes generate O<sub>2</sub> or where processes require further loading of material after inertisation.

#### **Layout of distillation condensers**

BAT is to minimise the exhaust gas volume flows from distillations by optimising the layout of the condenser.

#### **Liquid addition to vessels, minimisation of peaks**

BAT is to carry out liquid addition to vessels as bottom feed or with dip-leg, unless reaction chemistry and/or safety considerations make it impractical. In such cases, the addition of liquid as top feed with a pipe directed to the wall reduces splashing and hence, the organic load in the displaced gas. If both solids and an organic liquid are added to a vessel, BAT is to use solids as a blanket in circumstances where the density difference promotes the reduction of the organic load in the displaced gas, unless reaction chemistry and/or safety considerations make it impractical. BAT is to minimise the accumulation of peak loads and flows and related emission concentration peaks by, e.g. optimisation of the production matrix and application of smoothing filters.

#### **Alternative techniques for product work-up**

BAT is to avoid mother liquors with high salt content or to enable the work-up of mother liquors by the application of alternative separation techniques, e.g. membrane processes, solvent-based processes, reactive extraction, or to omit intermediate isolation. BAT is to apply countercurrent product washing where the production scale justifies the introduction of the technique.

**Vacuum, cooling and cleaning**

BAT is to apply water-free vacuum generation by using, e.g. dry running pumps, liquid ring pumps using solvents as the ring medium or closed cycle liquid ring pumps. However, where the applicability of these techniques is restricted, the use of steam injectors or water ring pumps is justified. For batch processes, BAT is to establish clear procedures for the determination of the desired end point of the reaction. BAT is to apply indirect cooling. However, indirect cooling is not applicable for processes which require the addition of water or ice to enable safe temperature control, temperature jumps or temperature shock. Direct cooling can also be required to control “run away” situations or where there are concerns about blocking heat-exchangers. BAT is to apply a pre-rinsing step prior to rinsing/cleaning of equipment to minimise organic loads in wash-waters. Where different materials are frequently transported in pipes, the use of pigging technology represents another option to reduce product losses within cleaning procedures.

**Management and treatment of waste streams****Mass balances and analysis of waste streams**

BAT is to establish mass balances for VOCs (including CHCs), TOC or COD, AOX or EOX (Extractable Organic Halogen) and heavy metals on a yearly basis. BAT is to carry out a detailed waste stream analysis in order to identify the origin of the waste stream and a basic data set to enable management and suitable treatment of exhaust gases, waste water streams and solid residues. BAT is to assess at least the parameters given in Table I for waste water streams, unless the parameter can be seen as irrelevant from a scientific point of view.

Parameter	
Volume per batch	Standard
Batches per year	
Volume per day	
Volume per year	
COD or TOC	
BOD <sub>5</sub>	
pH	
Bioeliminability	
Biological inhibition, including nitrification	
AOX	
CHCs	
Solvents	
Heavy metals	
Total N	
Total P	
Chloride	
Bromide	
SO <sub>4</sub> <sup>2-</sup>	
Residual toxicity	

**Table I: Parameters for the assessment of waste water streams**

**Monitoring of emissions to air**

Emission profiles should be recorded instead of levels derived from short sampling periods. Emission data should be related to the operations responsible. For emissions to air, BAT is to monitor the emission profile which reflects the operational mode of the production process. In the case of a non-oxidative abatement/recovery system, BAT is to apply a continuous monitoring system (e.g. Flame Ionisation Detector, FID), where exhaust gases from various processes are treated in a central recovery/abatement system. BAT is to individually monitor substances with ecotoxicological potential if such substances are released.

### **Individual volume flows**

BAT is to assess the individual exhaust gas volume flows from process equipment to recovery/abatement systems.

### **Re-use of solvents**

BAT is to re-use solvents as far as purity requirements allow. This is carried out by using the solvent from previous batches of a production campaign for future batches, collecting spent solvents for on-site or off-site purification and re-use, or collecting spent solvents for on-site or off-site utilisation of the calorific value.

### **Selection of VOC treatment techniques**

One or a combination of techniques can be applied as a recovery/abatement system for a whole site, an individual production building, or an individual process. This depends on the particular situation and affects the number of point sources. BAT is to select VOC recovery and abatement techniques according to the flow scheme in Figure I.

### **Non-oxidative VOC recovery or abatement: achievable emission levels**

Where non-oxidative VOC recovery or abatement techniques are applied, BAT is to reduce emissions to the levels given in Table II.

### **Thermal oxidation/incineration or catalytic oxidation: achievable emission levels**

Where thermal oxidation/incineration or catalytic oxidation are applied, BAT is to reduce VOC emissions to the levels given in Table III.

### **Recovery/abatement of NO<sub>x</sub>**

For thermal oxidation/incineration or catalytic oxidation, BAT is to achieve the NO<sub>x</sub> emission levels given in Table IV and, where necessary, to apply a DeNO<sub>x</sub> system (e.g. SCR or SNCR) or two stage combustion to achieve such levels. For exhaust gases from chemical production processes, BAT is to achieve the NO<sub>x</sub> emission levels given in Table IV and, where necessary to apply treatment techniques such as scrubbing or scrubber cascades with scrubber media such as H<sub>2</sub>O and/or H<sub>2</sub>O<sub>2</sub> to achieve such levels. Where NO<sub>x</sub> from chemical processes is absorbed from strong NO<sub>x</sub> streams (about 1000 ppm and higher) a 55 % HNO<sub>3</sub> can be obtained for on-site or off-site re-use. Often, exhaust gases containing NO<sub>x</sub> from chemical processes also contain VOCs and can be treated in a thermal oxidiser/incinerator, e.g. equipped with a DeNO<sub>x</sub> unit or built as a two stage combustion (where already available on-site).

### **Recovery/abatement of HCl, Cl<sub>2</sub>, HBr, NH<sub>3</sub>, SO<sub>x</sub> and cyanides**

HCl can be efficiently recovered from exhaust gases with high HCl concentrations, if the production volume justifies the investment costs for the required equipment. Where HCl recovery is not preceded by VOC removal, potential organic contaminants (AOX) have to be considered in the recovered HCl. BAT is to achieve the emission levels given in Table VI and, where necessary, to apply one or more scrubbers using suitable scrubbing media.

### **Removal of particulates**

Particulates are removed from various exhaust gases. The choice of recovery/abatement systems depends strongly on the particulate properties. BAT is to achieve particulate emission levels of 0.05 – 5 mg/m<sup>3</sup> or 0.001 – 0.1 kg/hour and, where necessary, to apply techniques such as bag filters, fabric filters, cyclones, scrubbing, or wet electrostatic precipitation (WESP) in order to achieve such levels.

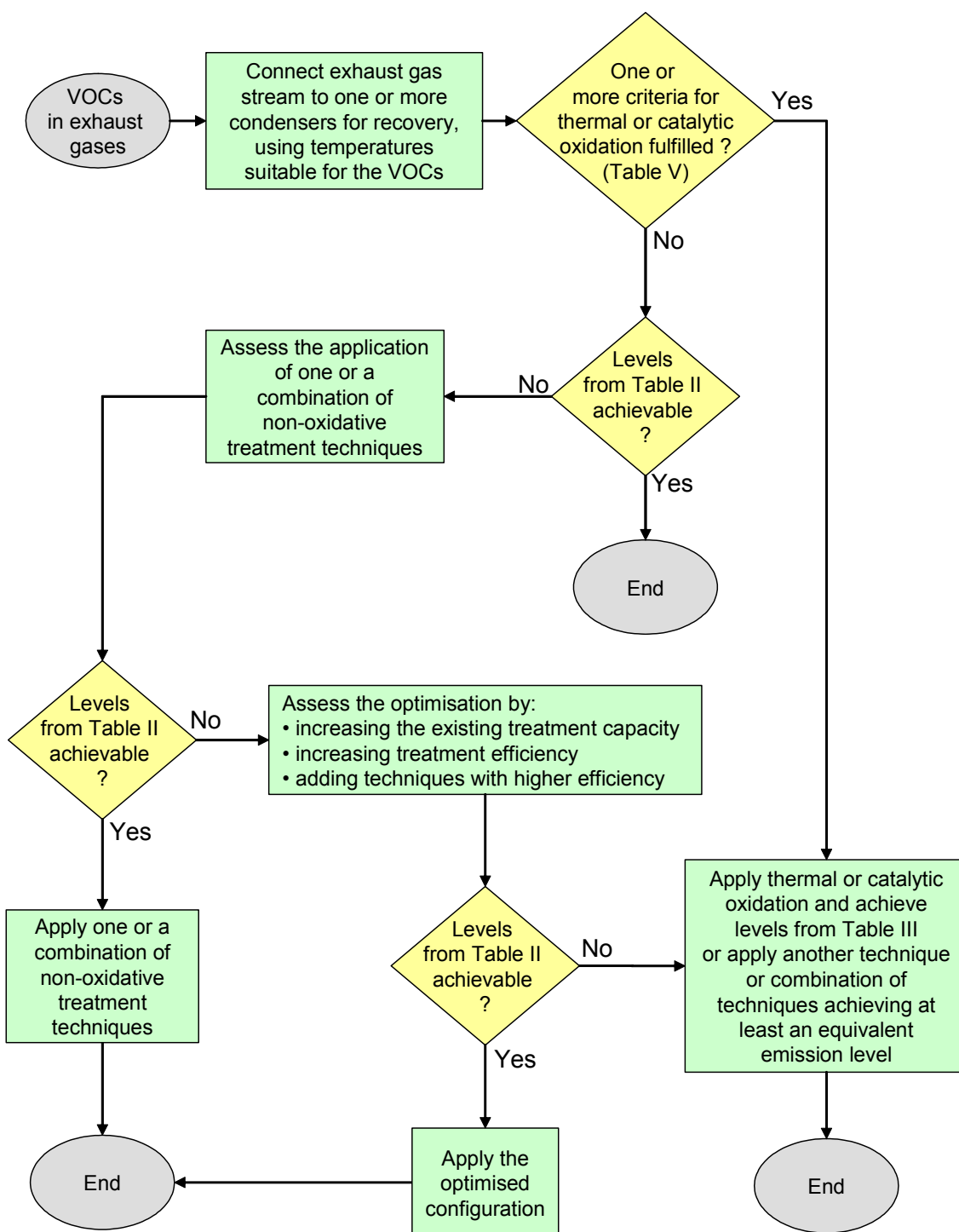


Figure I: BAT for the selection of VOC recovery/abatement techniques

Parameter	Average emission level from point sources*
Total organic C	0.1 kg C/hour or 20 mg C/m <sup>3</sup> **
* The averaging time relates to the emission profile, the levels relate to dry gas and Nm <sup>3</sup>	
** The concentration level relates to volume flows without dilution by, e.g. volume flows from room or building ventilation	

Table II: BAT associated VOC emission levels for non-oxidative recovery/abatement techniques

Thermal oxidation/incineration or catalytic oxidation	Average mass flow kg C/hour		Average concentration mg C/m <sup>3</sup>
Total organic C	<0.05	or	<5
The averaging time relates to the emission profile, levels relate to dry gas and Nm <sup>3</sup>			

**Table III: BAT associated emission levels for total organic C for thermal oxidation/incineration or catalytic oxidation**

Source	Average kg/hour <sup>*</sup>		Average mg/m <sup>3</sup> <sup>*</sup>	Comment
Chemical production processes, e.g. nitration, recovery of spent acids	0.03 – 1.7	or	7 – 220 <sup>**</sup>	The lower end of the range relates to low inputs to the scrubbing system and scrubbing with H <sub>2</sub> O. With high input levels, the lower end of the range is not achievable even with H <sub>2</sub> O <sub>2</sub> as the scrubbing medium
Thermal oxidation/incineration, catalytic oxidation	0.1 – 0.3		13 – 50 <sup>***</sup>	
Thermal oxidation/incineration, catalytic oxidation, input of nitrogenous organic compounds			25 – 150 <sup>***</sup>	Lower range with SCR, upper range with SNCR
<sup>*</sup> NO <sub>x</sub> expressed as NO <sub>2</sub> , the averaging time relates to the emission profile <sup>**</sup> Levels relate to dry gas and Nm <sup>3</sup> <sup>***</sup> Levels relate to dry gas and Nm <sup>3</sup>				

**Table IV: BAT associated NO<sub>x</sub> emission levels**

	Selection criteria
<b>a</b>	The exhaust gas contains very toxic, carcinogenic or cmr category 1 or 2 substances, or
<b>b</b>	autothermal operation is possible in normal operation, or
<b>c</b>	overall reduction of primary energy consumption is possible in the installation (e.g. secondary heat option)

**Table V: Selection criteria for catalytic and thermal oxidation/incineration**

Parameter	Concentration		Mass flow
HCl	0.2 – 7.5 mg/m <sup>3</sup>	or	0.001 – 0.08 kg/hour
Cl <sub>2</sub>	0.1 – 1 mg/m <sup>3</sup>		
HBr	<1 mg/m <sup>3</sup>		
NH <sub>3</sub>	0.1 – 10 mg/m <sup>3</sup>		0.001 – 0.1 kg/hour
NH <sub>3</sub> from SCR or SNCR	<2 mg/m <sup>3</sup>		<0.02 kg/hour
SO <sub>x</sub>	1 – 15 mg/m <sup>3</sup>		0.001 – 0.1 kg/hour
Cyanides as HCN	1 mg/m <sup>3</sup>		3 g/hour

**Table VI: BAT associated emission levels for HCl, Cl<sub>2</sub>, HBr, NH<sub>3</sub>, SO<sub>x</sub> and cyanides**



**Typical waste water streams for segregation and selective pretreatment**

BAT is to segregate and pretreat or dispose of mother liquors from halogenations and sulphochlorinations. BAT is to pretreat waste water streams containing biologically active substances at levels which could pose a risk either to a subsequent waste water treatment or to the receiving environment after discharge. BAT is to segregate and collect separately spent acids, e.g. from sulphonations or nitrations for on-site or off-site recovery or to apply BAT about pretreatment of refractory organic loadings.

**Pretreatment of waste water streams with refractory organic loadings**

BAT is to segregate and pretreat waste water streams containing relevant refractory organic loadings according to this classification: Refractory organic loading is not relevant if the waste water stream shows a bioeliminability of greater than about 80 - 90 %. In cases with lower bioeliminability, the refractory organic loading is not relevant if it is lower than the range of about 7.5 - 40 kg TOC per batch or per day. For the segregated waste water streams, BAT is to achieve overall COD elimination rates for the combination of pretreatment and biological treatment of >95 %.

**Recovery of solvents from waste water streams**

BAT is to recover solvents from waste water streams for on-site or off-site re-use, where the costs for biological treatment and purchase of fresh solvents are higher than the costs for recovery and purification. This is carried out by using techniques such as stripping, distillation/rectification, extraction or combinations of such techniques. BAT is to recover solvents from waste water streams in order to use the calorific value if the energy balance shows that overall natural fuel can be substituted.

**Removal of halogenated compounds from waste water streams**

BAT is to remove purgeable CHCs from waste water streams, e.g. by stripping, rectification or extraction and to achieve levels given in Table VII. BAT is to pretreat waste water streams with significant AOX loads and to achieve the AOX levels given in Table VII in the inlet to the on-site biological Waste Water Treatment Plant (WWTP) or in the inlet to the municipal sewerage system.

**Removal of heavy metals from waste water streams**

BAT is to pretreat waste water streams containing significant levels of heavy metals or heavy metal compounds from processes where they are used deliberately and to achieve the heavy metal concentrations given in Table VII in the inlet to the on-site biological WWTP or in the inlet to the municipal sewerage system. If equivalent removal levels can be demonstrated in comparison with the combination of pretreatment and biological waste water treatment, heavy metals can be eliminated from the total effluent using only the biological waste water treatment process, provided that the biological treatment is carried out on-site and the treatment sludge is incinerated.

Parameter	Yearly average	Unit	Comment
AOX	0.5 - 8.5	mg/l	The upper range relates to cases where halogenated compounds are processed in numerous processes and the corresponding waste water streams are pretreated and/or where the AOX is very bioeliminable
Purgeable CHCs	<0.1		Alternatively achieve a sum concentration of <1 mg/l in the outlet from pretreatment
Cu	0.03 - 0.4		The upper ranges result from the deliberate use of heavy metals or heavy metal compounds in numerous processes and the pretreatment of waste water streams from such use
Cr	0.04 - 0.3		
Ni	0.03 - 0.3		
Zn	0.1 - 0.5		

**Table VII: BAT associated levels in the inlet to the on-site biological WWTP or in the inlet to the municipal sewerage system**

**Free cyanides**

BAT is to recondition waste water streams containing free cyanides in order to substitute raw materials where technically possible. BAT is to pretreat waste water streams containing significant loads of cyanides and to achieve a cyanide level of 1 mg/l or lower in the treated waste water stream or to enable safe degradation in a biological WWTP.

**Biological waste water treatment**

BAT is to treat effluents containing a relevant organic load, such as waste water streams from production processes, rinsing and cleaning water, in a biological WWTP. BAT is to ensure that the elimination in a joint waste water treatment is overall not poorer than in the case of on-site treatment. For biological waste water treatment, COD elimination rates of 93 – 97 % are typically achievable as a yearly average. It is important that a COD elimination rate cannot be understood as a standalone parameter, but is influenced by the production spectrum (e.g. production of dyes/pigments, optical brighteners, aromatic intermediates which create refractory loadings in most of the waste water streams on a site), the degree of solvent removal and the degree of pretreatment of refractory organic loadings. Depending on the individual situation, retrofitting of the biological WWTP is required in order to adjust, e.g. treatment capacity or buffer volume or the application of a nitrification/denitrification or a chemical/mechanical stage. BAT is to take full advantage of the biological degradation potential of the total effluent and to achieve BOD elimination rates above 99 % and yearly average BOD emission levels of 1 - 18 mg/l. The levels relate to the effluent after biological treatment without dilution, e.g. by mixing with cooling water. BAT is to achieve the emission levels given in Table VIII.

**Monitoring of the total effluent**

BAT is to regularly monitor the total effluent to and from the biological WWTP. BAT is to carry out regular biomonitoring of the total effluent after the biological WWTP where substances with ecotoxicological potential are handled or produced with or without intention. Where residual toxicity is identified as a concern (e.g. where fluctuations of the performance of the biological WWTP can be related to critical production campaigns), BAT is to apply online toxicity monitoring in combination with online TOC measurement.

Parameter	Yearly averages*		Comment
	Level	Unit	
COD	12 - 250	mg/l	
Total P	0.2 - 1.5		The upper range results from the production of mainly compounds containing phosphorus
Inorganic N	2 - 20		The upper range results from production of mainly organic compounds containing nitrogen or from, e.g. fermentation processes
AOX	0.1 - 1.7		The upper range results from numerous AOX relevant productions and pretreatment of waste water streams with significant AOX loads
Cu	0.007 - 0.1		The upper ranges result from the deliberate use of heavy metals or heavy metal compounds in numerous processes and the pretreatment of waste water streams from such use
Cr	0.004 - 0.05		
Ni	0.01 - 0.05		
Zn	– 0.1		
Suspended solids	10 - 20		
LID <sub>F</sub>	1 - 2		Dilution factor
LID <sub>D</sub>	2 - 4		
LID <sub>A</sub>	1 - 8		
LID <sub>L</sub>	3 - 16		
LID <sub>EU</sub>	1.5		
* The levels relate to the effluent after biological treatment without dilution, e.g. by mixing with cooling water			

**Table VIII: BAT for emissions from the biological WWTP**

#### **IV. Concluding remarks**

The information exchange on Best Available Techniques for the Manufacture of Organic Fine Chemicals was carried out from 2003 to 2005. The information exchange process was successful and a high degree of consensus was reached during and following the final meeting of the Technical Working Group. No split views were recorded. However, it has to be noted that increasing confidentiality concerns represented a considerable obstacle throughout the work.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the Preface of this document).