medichem

Annex I: Comparison of processes at Medichem with BREF for Organic Fine Chemicals (published August 2006).

Aspect of BAT	BAT	Status at Medichem
Environmental management	Environmental management system (in-house or customised)	Implemented; ISO 14001.
Integration of environmental considerations into process development	To provide an auditable trail for the integration of environmental, health and safety considerations into process development.	Existence of the standard operating procedure (SOP) "Environmental Protection, Health and Safety Criteria in the Design and Development of Processes" which is fully implemented.
	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.	Above-mentioned SOP contains a procedure for full assessment of the processes which are then straightforwardly scaled-up in the production. In addition, there are several SOPs taking into account deviations of the processes and the operation of the plant.
	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.	A series of related SOPs, regularly carried out risk assessments (the last was on April 2009), an initial training plan for each employee as well as annual training sessions together with the concept of "missed" incidents are fully implemented and maintained in order to limit risks from handling and storage of hazardous substances.
	To design new plants in such a way that emissions are minimised.	Implemented.
	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.	Implemented.
	To enable leakages to be quickly and reliably recognised.	Implemented (relevant SOP).
	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.	Implemented.

Aspect of BAT	BAT	Status at Medichem
Enclosure of sources and airtightness of equipment	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.	Implemented. Drying is carried out in a closed circuit including condensers for solvent recovery.
	To use recirculation of process vapours where purity requirements allow this.	Implemented. Existence of distillation of vapours used back in the process (aka “reflux” process).
	To minimise the volume flow, to close any unnecessary openings in order to prevent air being sucked to the gas collection system via the process equipment.	Implemented. Once the reactor is loaded, the reactor and other equipment are fully airtight. Use of inert gas (nitrogen) due to safety purposes.
	To ensure the airtightness of process equipment, especially of vessels.	Ibid
	To apply shock inertisation instead of continuous inertisation. Still, continuous inertisation has to be accepted due to safety requirements, e.g. where processes generate O2 or where processes require further loading of material after inertisation.	Implemented. Inertisation is carried out by replacing created vacuum with nitrogen which is then continuously added at low flow rate.
Layout of distillation condensers	BAT is to minimise the exhaust gas volume flows from distillations by optimising the layout of the condenser.	Implemented. All lines of exhaust gas are directed to one discharge point via scrubber treatment.
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.	Implemented. Loading of solids and liquids is carried out in inert atmosphere and in a way to prevent any splashing of liquids and creation of dusts, in order to ensure safe operation.
	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.	Loading is defined by the approved and validated master batch (operating procedure of the process itself). Optimisation of loadings of various processes is not relevant under present level of production (relatively low level of production and number of reactors).

Aspect of BAT	BAT	Status at Medichem
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.	Implemented. This issue is addressed during research and development. In addition, mother liquors are concentrated via distillation to recover solvents.
	BAT is to apply countercurrent product washing where the production scale justifies the introduction of the technique.	Not appropriate. Product washing is integrated with the other unit operations in order to make product loss negligible.
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.	Implemented. Use of close circuit liquid (oil) vacuum pumps to generate water-free vacuum.
	For batch processes, BAT is to establish clear procedures for the determination of the desired end point of the reaction.	Implemented. Existence of approved and validated master batch document
	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.	Implemented. Indirect cooling with glycol for the main process equipment and with glycol, water and sanitary oil for condensers. All the systems of cooling operated as a closed systems.
	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.	Implemented. Pre-rinsing by solvents is carried out during transfer of product in order to reduce product loss and minimise organic load of washing waters and therefore significantly reduce the amount of water used for cleaning.
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.	Implemented. Balance for VOCs has been estimated on the yearly basis; COD is checked on a regular basis (before each discharge to the sewer). AOX and heavy metals are not relevant.
	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.	Implemented. Distinction between wastewaters to be treated in the own treatment plant and liquid wastes to be exported is made according to the contaminant load and applicable legal requirements.

Aspect of BAT	BAT	Status at Medichem
	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. ***Standard parameters*** Volume per batch Batches per year Volume per day Volume per year COD or TOC BOD5 pH Bioeliminability Biological inhibition, including nitrification ***Other parameters (where they are expected)*** AOX CHCs Solvents Heavy metals Total N Total P Chloride Bromide SO42- Residual toxicity	The underlined parameters are assessed. Heavy metals are not relevant. Other parameters are not monitored, according to the agreement with the regulatory authorities.
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.	Implemented as per current permit. In the case of change in production, the monitoring of emissions will be changed accordingly.
	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.	Not applicable due to type of installed equipment, nature of operation and internal procedures in place.
	BAT is to individually monitor substances with ecotoxicological potential if such substances are released.	Not applicable.

Aspect of BAT	BAT	Status at Medichem
Individual volume flows	BAT is to assess the individual exhaust gas volume flows from process equipment to recovery/abatement systems.	Not applicable.
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.	Implemented.
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.	Implemented. VOC recovery and abatement techniques are selected according to the flow scheme in Figure 1 with the assumption that the emission level in the Table II can be achieved with further optimisation of the scrubber operation (taking into account the accuracy of available monitoring technique).
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.	The ELV in the permit is 150 mgC/Nm^3, whereas BAT is 20 mgC/Nm^3. The latest results indicate that the used abatement technique provide the ELV much lower than the applicable legal requirements. Further reduction of the ELV is not economically feasible.
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.	Not applicable. Thermal oxidation/incineration or catalytic oxidation are not applied.
Recovery/abatement of NOX	For thermal oxidation/incineration or catalytic oxidation, BAT is to achieve the NOX emission levels given in Table IV and, where necessary, to apply a DeNOX system (e.g. SCR or SNCR) or two stage combustion to achieve such levels.	Not applicable. Thermal oxidation/incineration or catalytic oxidation are not applied.

Aspect of BAT	BAT	Status at Medichem
	For exhaust gases from chemical production processes, BAT is to achieve the NOX emission levels given in Table IV and, where necessary to apply treatment techniques such as scrubbing or scrubber cascades with scrubber media such as H2O and/or H2O2 to achieve such levels. Where NOX from chemical processes is absorbed from strong NOX streams (about 1000 ppm and higher) a 55 % HNO3 can be obtained for onsite or off-site re-use. Often, exhaust gases containing NOX from chemical processes also contain VOCs and can be treated in a thermal oxidiser/incinerator, e.g. equipped with a DeNOX unit or built as a two stage combustion (where already available on-site).	Not applicable. The level of NOX in exhaust gases from chemical production processes is negligible.
Recovery/abatement of HCl, Cl2, HBr, NH3, SOx 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.	Currently, HCl gas is used in only two processes. A scrubber system loaded with NaOH solution is used to neutralise excess gas. Aqueous solutions of HCl, HBr and NH3 are used in small quantities (packed in small drums) with negligible fugitive emissions.
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/m3 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.	Implemented.
Typical waste water streams for segregation and selective pretreatment	BAT is to segregate and pretreat or dispose of mother liquors from halogenations and sulphochlorinations.	Even though we do not carry out any halogenations or sulphochlorinations, the present permit specifies that if halogenated solvent is generated, such waste would be segregated and treated separately.

Aspect of BAT	BAT	Status at Medichem
	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.	Not applicable.
	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.	Not applicable.
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 %.	Organic loads of the wastewaters in the WWTP are regularly monitored and segregation of wastewaters to be treated internally and liquid waste to be treated off-site is carried out accordingly.
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.	Implemented. Wherever possible and economically feasible, the solvents are recovered. Otherwise, the wastewater is collected as a liquid waste to be exported for off-site recovery. The recovery of solvents are emphasized by the objectives of the ISO14001 environmental management system.
	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.	Not applicable.
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.	Not applicable.
	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.	Not applicable.

Aspect of BAT	BAT	Status at Medichem
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.	Not applicable.
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.	No such materials. Not applicable.
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.	Not applicable at the present level of production – at this moment it is more economically feasible to collect the wastewaters are a liquid waste and export them for treatment than to invest in a biological WWTP

Aspect of BAT	BAT	Status at Medichem
	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.	The present average COD level represents a compromise between on-site and off-site treatment taking into account present legal requirements. Waste solvents and high COD load wastewaters are always separated and treated off-site.
	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.	Same as COD.
Monitoring of the total effluent	BAT is to regularly monitor the total effluent to and from the biological WWTP.	Not applicable.
	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.	Not applicable.
	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.	Not applicable.

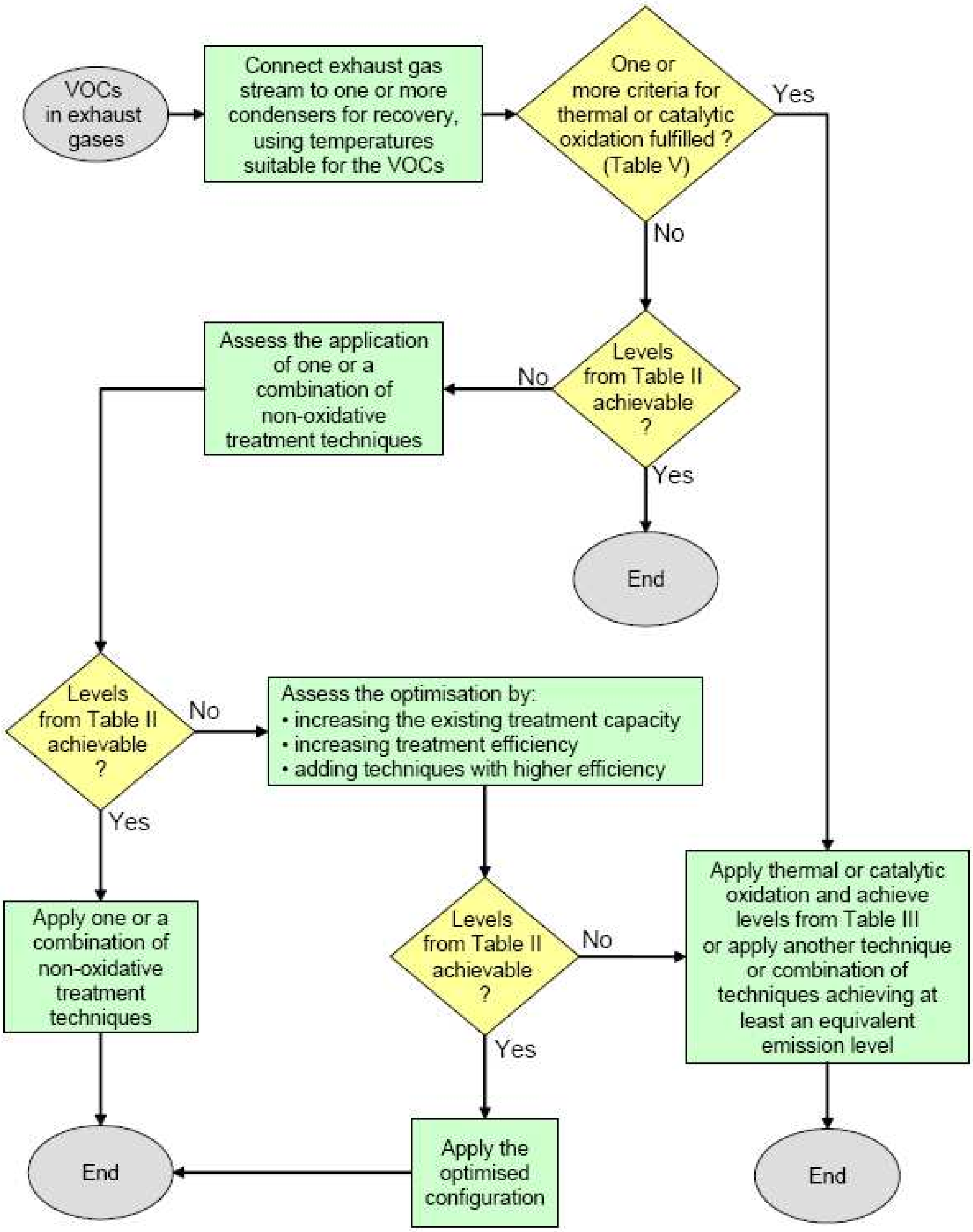

Figure I: BAT for the selection of VOC recovery/abatement techniques

Parameter	Average emission level from point sources*
Total organic C	0.1 kg C/hour or 20 mg C/m^3**
* The averaging time relates to the emission profile, the levels relate to dry gas and Nm^3 ** 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/m³
Total organic C	<0.05	or	<5
The averaging time relates to the emission profile, levels relate to dry gas and Nm^3			

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

Source	Average kg/hour*		Average mg/m³*	Comment
Chemical production processes, e.g. nitration, recovery of spent acids	0.03 – 1.7	or	7 – 220**	The lower end of the range relates to low inputs to the scrubbing system and scrubbing with H_2O. With high input levels, the lower end of the range is not achievable even with H_2O_2 as the scrubbing medium
Thermal oxidation/incineration, catalytic oxidation	0.1 – 0.3	or	13 – 50***	
Thermal oxidation/incineration, catalytic oxidation, input of nitrogenous organic compounds		or	25 – 150***	Lower range with SCR, upper range with SNCR

* NO_X expressed as NO_2, the averaging time relates to the emission profile
** Levels relate to dry gas and Nm^3
*** Levels relate to dry gas and Nm^3

Table IV: BAT associated NO_x emission levels

	Selection criteria
a	The exhaust gas contains very toxic, carcinogenic or cmr category 1 or 2 substances, or
b	autothermal operation is possible in normal operation, or
c	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/m³	or	0.001 – 0.08 kg/hour
Cl_2	0.1 – 1 mg/m³	or	
HBr	<1 mg/m³	or	
NH_3	0.1 – 10 mg/m³	or	0.001 – 0.1 kg/hour
NH_3 from SCR or SNCR	<2 mg/m³	or	<0.02 kg/hour
SO_x	1 – 15 mg/m³	or	0.001 – 0.1 kg/hour
Cyanides as HCN	1 mg/m³	or	3 g/hour

Table VI: BAT associated emission levels for HCl, Cl_2, HBr, NH_3, SO_x and cyanides

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

	Yearly averages*		
Parameter	**Level**	**Unit**	**Comment**
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_F	1 - 2	Dilution factor	Toxicity is also expressed as aquatic toxicity (EC_{50} levels)
LID_D	2 - 4		
LID_A	1 - 8		
LID_L	3 - 16		
LID_{EU}	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