Guidance: Wastewater Discharge from Crop Protection Product Manufacturing

Crop Life International (CLI): Water Risk Assessment Project

CropLife INTERNATIONAL

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1 INTRODUCTION

Water is an increasingly scarce resource. A major challenge for households, agriculture and industry will be the sustainable supply of water, seriously threatening economic and societal development.

Water is also of fundamental importance in the crop protection industry. It is used as a coolant, solvent, and cleaning agent, as well as to formulate crop protection products.

CropLife International member companies are committed to a responsible use of water along the entire value chain and especially in production sites' water catchment areas. They are fully aware of their responsibility for protecting the environment and therefore apply proper wastewater management.

Generally, the key focus regarding water management is to minimize wastewater volumes and contaminant loads in production processes, and to reuse water internally as far as possible. Even with technical measures and optimized operating methods it is hardly possible to completely avoid the formation of wastewater streams. These wastewater streams require treatment before being discharged to minimize their environmental impact. Unintentional release of contaminated wastewater and the pollution of surface or groundwater must be prevented by establishing water protection and "pollution prevention" concepts. These concepts were described in a CropLife International Guidance document [1].

This document addresses the intentional discharge of wastewater. It is intended as a Technical Guidance for the CP Product Manufacturing Industry to develop wastewater discharge strategies and mitigate the potential impacts of contaminants in wastewater from manufacturing operations. Liquid waste in any form is not in the scope of this guidance document (see Section 2.1).

Wastewater management concepts, wastewater treatment technologies and monitoring strategies are described. However, not all available techniques are captured, and technical handling is not discussed in detail. Techniques, risk assessment tools and concepts need to be adapted to local requirements and implemented based on company-specific procedures.

The purpose of this guidance document is to address the following aspects of wastewater discharge:

- Main principles of wastewater management and risk assessment
- Wastewater treatment concepts and applicability of current technologies
- Definition of discharge compliance criteria and appropriate controls
- Development of wastewater discharge monitoring strategies

2 CONCEPT OF WASTEWATER MANAGEMENT AND RISK ASSESSMENT

Environmental Impact Assessment (EIA) and Environmental Risk Assessment (ERA) are both important tools used to evaluate and manage potential environmental impacts and risks associated with human activities. While they share similarities, there are distinct differences between the two. For the purposes of implementing strategies associated with this document, both should be considered.

	Environmental Impact Assessment (EIA)	Environmental Risk Assessment (ERA)
Purpose	EIA is conducted to assess and predict the potential environmental effects of proposed projects, policies, or developments before they are implemented. Its primary aim is to provide information for decision making and ensure that potential adverse environmental impacts are identified and mitigated or avoided.	ERA focuses on assessing and quantifying the potential risks posed by specific materials, activities, or situations to the environment. It aims to provide an understanding of the likelihood and consequences of adverse effects, facilitating risk management and decision-making.
Scope	EIA evaluates a wide range of potential impacts, including ecological, social, and economic factors. It considers both direct and indirect effects of the proposed activity on the environment, as well as cumulative effects that may result from multiple projects in the same area.	ERA focuses specifically on the potential risks associated with specific hazards or stressors, such as chemicals, pollutants, or industrial processes. It assesses the likelihood of exposure and the potential ecological or human health effects resulting from that exposure.
Focus	EIA examines the overall changes to the environment, such as changes in land use, air and water quality, biodiversity, human health, and socio-economic aspects. It provides a comprehensive assessment of the potential impacts across various environmental components.	ERA concentrates on the analysis of risks, including hazard identification, exposure assessment, and toxicity assessment. It quantifies and characterizes the risks, considering factors such as dose-response relationships, exposure pathways, and the vulnerability of receptors (both environmental and human).
Timeframe	EIA is typically conducted during the early stages of project planning and decision-making processes, often prior to obtaining necessary permits or approvals. It aims to integrate environmental considerations into the project design and identify appropriate mitigation measures.	ERA can be conducted at different stages of a project or activity's lifecycle, including during initial planning, operation, or even after the release of a substance. It is an ongoing process that can be revisited and updated as new information becomes available or circumstances change.

For the purposes of this document, we are dealing solely with wastewater risk to minimize environmental impact. Wastewater risk assessment is described in more detail in Section 2.3.

2.1 UNDERSTANDING WASTEWATER STREAMS

At a typical production site, there are various wastewater streams from different sources and with different types and levels of contamination. Contaminant means any material that can cause harm to humans or any other living organism or damaging the environment when accidentally or deliberately introduced to air, water, or soil. In many cases, it can be beneficial to treat certain streams separately to reduce the efforts (e.g., cost, energy) required to meet compliance criteria.

Each manufacturing site should create an inventory of all relevant types of wastewater streams to decide on strategies for wastewater treatment and discharging which is based on the following criteria:

- Full compositions / chemical constituents (quantity / average / peak)
- Flow characteristics (quantity / average flow / peak)
- Physical / chemical characteristics
- Compliance criteria (regulatory standards, internally derived standards)
- Risk drivers

However, some wastewater streams need to be handled as liquid waste. This refers to highly polluted wastewater streams which are defined as hazardous waste by applicable regulation. Consequently, the definition of hazardous waste and the subsequent decision on disposal and/or recovery of waste must follow regulatory requirements applicable to the manufacturing site.

Liquid waste in any form is not in the scope of this guidance document and is excluded from the following discussion on wastewater streams.

Wastewater to be treated may contain contaminants (e.g., Active Ingredients of the plant protection products, intermediates, raw materials, solvents, auxiliaries, by-products). It must be treated in an appropriate manner (see Section 3) before being discharged into the receptor body e.g. surface water (sea, river) in compliance with limits and thresholds of national law and site permits.

At manufacturing sites, the wastewater is often discharged into a public sewer system or into the sewer system of an industrial park and then treated in a wastewater treatment plant of a community, or an industrial park. In these cases (and in case of direct discharge), limit values for wastewater at the point of discharge into the sewage system must be followed.

Discharge compliance criteria are discussed in Section 4.2.

There are two classifications of wastewater streams:

Wastewater to be treated is (potentially) contaminated water and includes the following wastewater streams. These wastewater streams typically require wastewater treatment to meet discharge criteria.

Process wastewater streams (see 4.6,[1]) come from the production processes (e.g., scrubber, distillations, cleaning and rinsing) and are considered contaminated water streams to be treated. Constituents (Active Ingredients, Substances of Very High Concern etc.), and physicochemical properties are outside of water quality standards, e.g.:

- Acidity or alkalinity at extremes (corrosive)
- Odors and turbidity
- Dissolved metals and suspended solids
- High salinity or toxicity
- Concentration limits of individual materials
- Chemical Oxygen Demand
- Nutrients

Firefighting water (see 4.10, [1]) has been used to extinguish an active fire in the unit or site. Due to its potential contamination, it is water to be treated or waste. Basic considerations in the Water Risk Assessment should include the volume of the firefighting water to be contained and treated. This volume should be estimated based on the site firefighting water system capability and the probable conditions during a specific scenario. Additionally, an estimate of the possible contamination contained in the used firefighting water and its treatability must be made in order to define the best treatment or disposal technique.

Sanitary wastewater is generated by sanitation and related activities and includes wastewater from toilets, sinks, showers, kitchens, and cleaning of general areas (unrelated to chemical handling or production). If and to which extent this wastewater streams needs to be included in the wastewater treatment depends on the separation between activities generating “domestic” sanitary wastewaters with those that may contain contamination from production-related chemicals (see 4.8, [1]).

Beside the regular wastewater streams also spillages and leakages must be considered in wastewater management and risk assessment. This implies that negative impacts by peak loads (caused by incidents or malfunctions) must be avoided through preventive water protection.

Wastewater NOT to be treated is noncontaminated water which can be directly discharged into the receiving surface water without wastewater treatment, if already meeting discharge limits as validated by analytical quantitation before. In many cases, this reduces the hydraulic load on the WWTP and the treatment costs. The following wastewater streams are included:

Cooling water (see 4.7, [1]) is used for carrying off heat from exothermic processes. Most often, this water is taken from a river, treated by filtration, distributed via a cooling water piping system, directed to heat exchangers and discharged back into the river. Cooling water can also be provided through recirculating systems (closed loop), in which the same volume of water is used repeatedly. Cooling water does not get into contact with any products or hazardous substances.

Boiler condensate or blow down are water streams not to be treated if uncontaminated and allowed for direct discharge by permit or regulation.

Stormwater runoff (see 4.9, [1]) is non-contaminated water from rain or snowmelt that is collected on impervious areas such as roofs, parking lots, roads, tank farms, production areas or unloading stations and is channelled through one or several dedicated storm water sewers and retention systems into a water body. It may be necessary to separate potentially contaminated and noncontaminated stormwater to avoid a hydraulic overload of the central wastewater treatment plant. This can be achieved with structural devices like first flush containments which should be designed to catch the first volume of precipitation onto a potentially contaminated area before an overflow into the non-treated wastewater system is possible.

2.2 WASTEWATER MANAGEMENT HIERARCHY OF CONTROLS

The facility will need to decide on wastewater management strategies that will be most effective for the site while considering the potential impacts to the environment.

The wastewater management hierarchy of controls provides a framework for implementing sustainable discharge practices by prioritizing actions that reduce or eliminate the generation of wastewater and its potential adverse impacts. The hierarchy follows a sequence of control measures, starting with the most preferred and effective options. Below are key elements of the wastewater management hierarchy of controls:

1. **Source Reduction and Minimization:** The first and most effective step is to reduce the generation of wastewater and contaminants at the source. This can be achieved through process modifications, improved operational practices, and implementing water conservation measures. By minimizing wastewater generation, the overall environmental impact can be significantly reduced.

2. **Reuse and Recycling:** The next step is to explore opportunities for reusing and recycling wastewater within the facility or in other appropriate applications. This may involve treating and reusing wastewater for non-potable purposes such as irrigation, industrial processes, or flushing. Recycling wastewater reduces the demand for freshwater resources and lessens the burden on wastewater treatment systems.

3. **Treatment and Pre-treatment:** If wastewater cannot be reduced or reused, it should be treated appropriately to remove or reduce contaminants before discharge. Depending on the nature of the contaminants, treatment technologies such as physical, chemical, and biological processes can be employed. Proper pre-treatment measures should also be implemented to remove specific pollutants that could interfere with subsequent treatment processes or pose risks to the environment. Refer to section 3 for additional details.

4. **Resource Recovery:** In line with sustainable practices, efforts should be made to recover valuable resources from wastewater. For example, nutrient recovery from wastewater can be carried out through processes such as anaerobic digestion or struvite precipitation. These recovered resources can be used as fertilizers or energy sources, contributing to a circular economy approach.

5. **Discharge:** If direct discharge to the environment is necessary, dispersion techniques can help minimize the impact on receiving waters. This may involve controlled discharge rates, mixing zones, or appropriate discharge locations and methods to ensure the effective dispersion of treated wastewater. Regular monitoring of the wastewater discharge, receiving waters, and relevant environmental indicators is crucial to assess the effectiveness of control measures and to ensure compliance with regulatory standards. Refer to section 4 for additional details.

By following the wastewater management hierarchy of controls, organizations can effectively minimize the generation of wastewater, optimize resource utilization, and reduce the environmental impact of wastewater discharge. The ultimate goal is to achieve sustainable wastewater management practices that prioritize pollution prevention, resource conservation, and protection of the receiving environment.

The wastewater management hierarchy of controls should be a dynamic process, promoting continuous improvement and innovation. This involves regularly reviewing and reassessing wastewater management practices, exploring new technologies and techniques, and staying updated with emerging best practices and regulatory requirements.

2.3 WASTEWATER RISK ASSESSMENT

The risk assessment model should be tailored to the specific contaminants, wastewater discharge characteristics, and local/federal regulatory requirements. Methods for measuring risk should consider likelihood, severity and/or frequency to measuring the impact, either quantitatively or qualitatively, using a rubric defined by the facility. The following steps are included in the risk assessment:

1. **Hazard Identification:** The first step in the risk assessment model is to identify the hazards associated with the contaminant present in wastewater discharge. This involves evaluating the physicochemical properties, toxicological data, and environmental fate of the materials. It is essential to consider any potential adverse effects on aquatic organisms, human health, and the ecosystem.

2. **Exposure Assessment:** The exposure assessment determines the magnitude and duration of exposure to the contaminant in the receiving waters. It involves analyzing the characteristics of the wastewater discharge, such as flow rate, volume, and concentration of the contaminants. Additionally, factors such as mixing, degradation, and bioaccumulation should be considered to estimate the actual exposure levels in the environment.

3. **Effect Assessment:** The effect assessment evaluates the potential effects of the contaminant on the environment and human health. This step includes reviewing available ecotoxicity data, such as acute and chronic toxicity studies on aquatic organisms and relevant information. All ecologically relevant endpoints should be considered, including but not limited to PNECs (Predicted No Effect Concentrations) and lethal concentrations as examples.

4. **Risk Quantification:** In this step, the estimated exposure levels from the exposure assessment are compared to the effect assessment data to quantify the potential risks associated with the wastewater discharge. The risk quantification may involve the use of various mathematical models to estimate the likelihood and severity of adverse effects. If the exposure exceeds the threshold levels determined from the effect assessment, there may be a risk of adverse effects on the environment or human health.

5. **Risk Characterization:** Once the risks are quantified, the risk characterization step involves summarizing and communicating the findings. This includes describing the nature and magnitude of the potential risks, identifying sensitive receptors or ecosystems, and highlighting any uncertainties or data gaps in the assessment. The risk characterization should be presented in a clear and concise manner, allowing stakeholders and decision-makers to understand the significance of the risks.

6. **Risk Mitigation:** Finally, based on the results of the risk assessment, appropriate risk mitigation measures should be identified and implemented to reduce or eliminate the identified risks. These measures may include implementing wastewater treatment technologies to remove or reduce the contaminants, implementing best management practices to minimize the release of contaminants, or exploring alternative raw materials that pose lower risks to the environment and human health.

2.4 WASTEWATER MANAGEMENT STRATEGY

When developing or modifying the wastewater strategy for a facility, prevention, reduction, recycling and reusing should drive discussion and decisions. General wastewater discharge strategies are described below.

- Consider opportunities for emission reduction. Emission reduction strategies for wastewater refer to the approaches and technologies used to minimize or eliminate the release of wastewater into the environment. These strategies aim to treat and reuse wastewater, thereby minimizing water consumption and protecting water resources. Some emission reduction strategies are identified below:
    - **Wastewater Treatment:** Implementing advanced wastewater treatment systems is crucial for achieving zero discharge. This includes primary, secondary, tertiary and quaternary treatment processes to remove contaminants such as solids, organic matter, nutrients, and toxic materials from wastewater. Advanced treatment technologies like membrane filtration, activated carbon adsorption, and reverse osmosis may be employed for thorough purification; examples and more detailed descriptions found in Section 5.
    - **Water Reuse:** Rather than discharging treated wastewater into water bodies, it can be reused for various purposes. Depending on the quality of the treated water, it can be used for irrigation, industrial processes, toilet flushing, or even for replenishing groundwater aquifers. Implementing appropriate filtration and disinfection processes ensures that the water meets the required standards for reuse.
    - **Water Conservation and Efficiency:** Reducing water consumption is a crucial aspect of zero discharge strategies. Implementing water-efficient technologies and practices such as low-flow fixtures, water recycling systems, and leak detection programs help minimize water usage and the generation of wastewater. This approach includes optimizing processes to reduce water usage in industrial operations, promoting water-saving habits and implementing efficient irrigation techniques.
    - **Industrial Symbiosis:** Industrial symbiosis involves collaborative efforts between industries to create a closed-loop system where one industry's waste becomes another industry's resource. By sharing resources like water, energy, and materials, industries can minimize their individual wastewater generation and reduce overall environmental impact.
    - **Zero Liquid Discharge (ZLD):** ZLD is an advanced wastewater treatment approach that aims to eliminate wastewater discharge completely. In ZLD systems, wastewater undergoes multiple treatment stages, including evaporation, crystallization, and solid-liquid separation. This process removes all water from the waste stream, leaving behind only solid residues that can be disposed of safely. The recovered water can be reused, and the remaining solids are often sent for proper disposal or used for beneficial applications like construction materials.
    - **Green Infrastructure:** Incorporating green infrastructure practices can help manage stormwater and reduce the amount of wastewater generated. Techniques like rainwater harvesting, bioswales, constructed wetlands, and permeable pavements promote natural filtration and groundwater recharge, reducing the load on wastewater treatment systems.

- **Education and Awareness:** Creating awareness among the general public, industries, and policymakers about the importance of zero discharge and the available technologies is crucial. Educating individuals about water conservation, sustainable practices, and the benefits of zero discharge can encourage behavioral changes and foster support for implementing such strategies

- On-site vs off-site treatment, or a combination of both will depend on many considerations. Some of the more common considerations are outlined below.
  - **On-Site Wastewater Treatment:**
    - **Cost:** On-site treatment systems can have lower initial costs compared to off-site options, especially for smaller-scale applications. However, ongoing maintenance, operational costs and investments should also be considered.
    - **Site suitability**: The suitability of the site for on-site treatment is crucial. Factors such as soil conditions, available space, and proximity to water bodies or sensitive areas need to be evaluated to ensure effective treatment and prevent environmental contamination.
    - **System design:** On-site treatment systems need to be designed to meet local regulations and standards. Factors such as wastewater volume, composition, and treatment requirements should be considered to select the appropriate system, such as septic tanks, aerobic treatment units, or constructed wetlands.
    - **Operation and maintenance:** On-site systems require regular operation and maintenance, including periodic inspections, sludge removal, and pump maintenance. Adequate training and resources should be allocated for the responsible management of the system.
  - **Off-Site Wastewater Treatment:**
    - **Centralized treatment:** Off-site treatment involves transporting wastewater from the source to a centralized treatment facility. This requires infrastructure for collection, conveyance, and treatment, which may involve higher capital costs compared to on-site systems.
    - **Scale and capacity**: Off-site treatment facilities are typically designed to handle larger volumes of wastewater from multiple sources. The scale and capacity of the facility should be considered to ensure it can handle current and future wastewater loads.
    - **Energy and resource use:** Off-site treatment facilities may require significant energy inputs for processes such as pumping, aeration, and sludge treatment. Considerations should be given to energy efficiency, renewable energy integration, and resource recovery opportunities.
    - **Environmental impact:** While off-site treatment facilities can achieve high levels of treatment, the transportation of wastewater to the facility can have environmental impacts, such as energy consumption and greenhouse gas emissions. The location of the facility should also consider the potential impact on surrounding ecosystems and communities.

- Discharge to the environment is a strategy that can be used, but there are various considerations to evaluate before choosing this path.
  - **Environmental Impact:** Discharging wastewater to the environment can have adverse effects on water bodies, ecosystems, and human health if not properly treated. Considerations should be given to the quality of the wastewater, its potential impacts on receiving waters, and the

vulnerability of local ecosystems.

- **Treatment Requirements:** Discharge to the environment may require some level of pre-treatment to meet regulatory standards. The type and extent of treatment will depend on the composition and characteristics of the wastewater and the applicable regulations.
- **Environmental Monitoring:** Monitoring the quality of the discharged wastewater and its impact on the environment is necessary to ensure compliance and detect any potential issues. Regular monitoring and reporting may be required to meet regulatory obligations.
- **Public Perception:** Discharge to the environment can be viewed unfavorably by the public, especially if there is a perceived risk to public health or environmental degradation. Engaging with stakeholders, addressing concerns, and maintaining transparency is essential.

- Accepting wastewater from third parties (inc. site tenants, neighbours, local communities). involves certain risks that need to be carefully considered, e.g.:
  - **Contaminant Composition:** The wastewater received from third parties may contain contaminants that are different from those typically present in the facility's own wastewater. This could include hazardous materials or pollutants that require specialized treatment methods or pose a higher risk to the treatment process or the environment.
  - **Inconsistent Quality and Characterization:** The quality and characterization of the incoming wastewater may vary, leading to challenges in maintaining consistent treatment performance. Fluctuations in flow rate, pH, temperature, and pollutant concentrations can impact the effectiveness of the treatment process and require additional process control measures.
  - **Treatment Capacity and Infrastructure:** Accepting third-party wastewater may put pressure on the facility's treatment capacity and infrastructure. Increased volumes or different treatment requirements may necessitate modifications or upgrades to the existing treatment system, which could involve significant costs and operational disruptions.
  - **Liability and Responsibility:** Accepting wastewater from third parties may introduce potential liability and responsibility issues. In case of any environmental damage, regulatory non-compliance, or accidents during transportation or transfer, the facility accepting the wastewater could be held accountable. Clear agreements and contracts detailing the responsibilities and liabilities of all parties involved are necessary to mitigate such risks.

2.5 PROGRAM IMPLEMENTATION MANAGEMENT

As part of any strategy, the facility will need to define aspects that impact wastewater discharge decisions. Using a Plan, Do, Check, Act (PDCA) model, the following aspects should be considered for inclusion in the facility's strategy:

- Gather and identify aspects
  - Map the site's scope. Facilities should identify all aspects that impact all wastewater streams, then identify measurements to track and trend the impacts. Having a comprehensive understanding will allow the facility to develop strategy and make informed decisions with all pertinent stakeholders. Consider regulatory landscape and stakeholder interests including:
    - Facility siting, including defined boundaries
      1. Site Water Balance: volume of water inputs, water used, water discharges with conveyance documentation
      2. List of Current Water Protection Measures: equipment such as tanks, ditches, trenches, containment, surge tanks and on-line monitoring
      3. Wastewater Retention Systems: Stormwater ponds, sumps, off-spec and equalization systems
      4. Administrative Controls and Procedures used to detect deviations from expected wastewater, cooling water and non-contaminated stormwater
      5. Control installations sluice gates, floodgates, weirs, underflows
      6. List of Hazardous Materials handled, including regulatory information
      7. Spill/Release History involving wastewater, cooling water, stormwater, and firewater
      8. Documentation of conveyances
      9. Documentation/management/review of material storage locations
    - Water related infrastructure, including piping network, owned or managed by site or parent organization or service provider
    - Water sources providing water to the site that are owned or managed by parent organization or third party
    - Water service provider
    - Discharge point, receiving water body/bodies and potential impacts
      1. Receptors
         - soils
         - groundwater
         - surface waters (rivers, lakes, the sea)
      2. Environmental sensitivity
         - ecology (flora and fauna, including microbiology) and sensitive habitats
         - neighbors and local communities
      3. Key risk drivers driving wastewater management strategy
         - ecological risks
         - human health risks from drinking water
         - contaminant accumulation in sediments etc.

    - facility layout
    - soil conditions
    - local regulation
  - Understand relevant stakeholders, their water related challenges and the site's ability to influence beyond its boundaries
  - Identify and collect site's water related data, including water governance, water quality, potential contamination sources and water related costs.
    - Water related incident response plans
    - Water balance including inflows, losses and outflows including annual variance (highs and lows), productions impacts, etc.
  - Understand current and future shared water challenges

- Commit and Plan
  - Document the process. Have a written policy/statement and document how the facility will maintain the program, including facility aspects.
  - Include and define program governance including key roles and responsibilities.

- Implement
  - Track status against plan and metrics/targets.

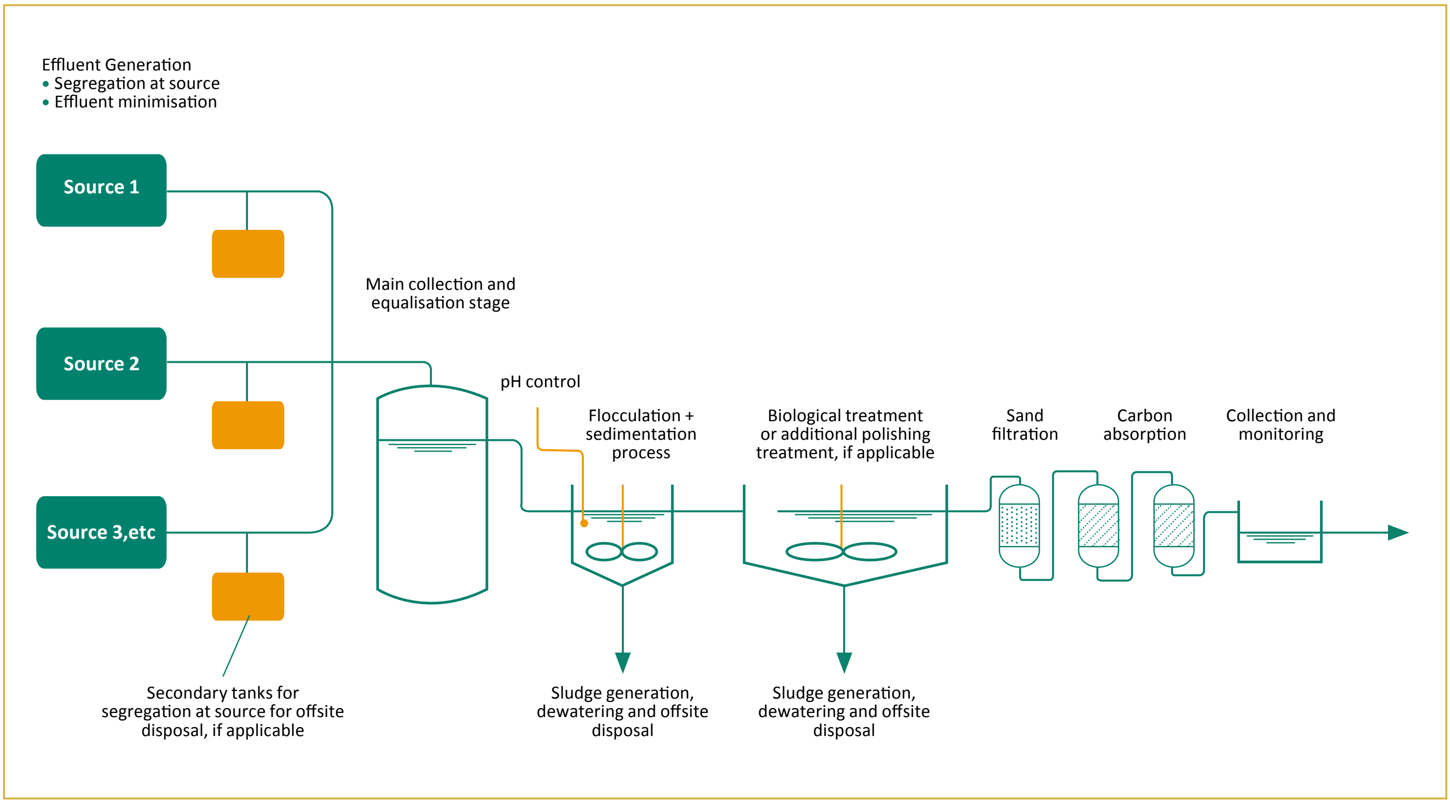
- Evaluate
  - Create a cadence and process for routine evaluation of all aspects of the program. Consider utilizing other stakeholders or industry experts as part of the evaluation process.

Facilities should identify all aspects that impact all wastewater streams, then identify measurements to track and trend the impacts. Having a comprehensive understanding will allow the facility to develop strategy and make informed decisions with all pertinent stakeholders.

3 DESIGN OF WASTEWATER TREATMENT PROCESSES

Wastewater treatment often requires a combination of treatment steps since none of the treatment steps can remove all kinds of contaminants.

As an example, a flowchart of the steps commonly included in a typical treatment system is presented below:



Furthermore, several treatment steps cannot be applied in the presence of certain contaminants. Therefore, the development of an effective treatment concept can be complex.

First step is defining the treatment concept to be applied to the wastewater stream we aim to treat. Some key aspects should be reviewed in this phase, for instance:

- The pollutants to be removed and treatment technologies to be used
- Potential risk to the current treatment system, if available (e.g., killing the microbiology)
- Segregation of critical streams
- Techniques to manage peaks in discharge (concentration and quantity)

In the table below is presented a list of current technologies and their applicability in wastewater treatment

Method	Technology	Applicability	Advantages	Weaknesses
Physical chemical	Precipitation	Dissolved material	Simplicity	Low cost
	Coagulation / Flocculation	Insoluble/ suspended material removal	Simplicity Low cost	Not useful for soluble materials
	Adsorption	Soluble (Organics and Inorganics)	Effective for a broad range of organic compounds	Adsorption rate is variable. Adsorber is consumed and regeneration can be complicated.
	Ion exchange	Soluble metals	Selective for metals	Moderate cost. Resins need to be regenerated
	Membrane Separation	Insoluble (organics and inorganics)	High efficiency for soluble material	High cost Clogging
	Advanced Oxidation Processes	Organic soluble	Process needs to be customized	Issues with high loads
Biological	Aerobic and/ or Anaerobic treatment	Organics, nitrogen compounds, phosphorus	Low to moderate cost	Issues with toxic compounds

Some details about technologies can be found below.

3.1 PRELIMINARY TREATABILITY TESTS

Preliminary treatability tests are performed to determine the best treatment to achieve the removal of contaminants required to comply with permit or agreement limits. They should be performed to test physical and chemical properties of relevance and their influence on treatment techniques.

3.2 WASTEWATER TREATMENT TECHNOLOGY

Wastewater treatment technologies and equipment must be properly selected and designed to ensure it complies with local regulations and minimizes potential environmental liabilities.

In this section we have some details about methods / technologies frequently used in treating crop protection manufacturing wastewaters:

3.2.1 FLOCCULATION TREATMENT

The flocculation treatment stage is a critical process for removing low solubility contaminants and those adsorbed on suspended solids. As a guide, the removal efficiency by flocculation combined with sludge separation typically account for about 10 to 50% of the overall chemical loading in the untreated effluent, depending on the chemicals and AIs used at the site. In some cases, removal efficiencies of up to 90% can be achieved. The choice and doses of the flocculating agents must be adapted to the effluent composition.

Note: as production campaigns can vary significantly depending on the products being formulated, it is important that flocculation trials are carried out regularly to determine the optimum chemical dosage to be applied during the treatment process. That is a challenge for instance for formulation plants that can change constantly the formulation portfolio.

3.2.2 FLOCCULATION TREATMENT

Biological treatment is often highly effective in removing a wide variety of soluble contaminants, including certain AIs. On average, a properly run biological unit can remove up to 60-80% of the remaining soluble chemical loading which normally cannot be removed by flocculation.
Biological treatment can be in the form of:

- Conventional Activated Sludge (CAS),
- Moving Bed Bio Reactors (MBBR), or
- Membrane Bio Reactors (MBR)

Factors that need to be considered when deciding between CAS, MBBR and MBR include space availability, chemical loadings, investment, operational and maintenance costs, level of automation and legal discharge requirements.

3.2.3 SAND FILTRATION

Sand filtration is commonly used before carbon filtration and is a critical component required to remove as much suspended solids from the effluent as possible to extend the life of the subsequent carbon filters. The sand filter needs to be properly designed and regularly backwashed to maintain its efficiency. Sand spent is potentially contaminated with chemicals so that it should be properly handled and managed as hazardous or non-hazardous waste depending on its characteristics and applicable local regulations.

3.2.4 CARBON ADSORPTION

In contrast to the sand filters, activated carbon is consumed during adsorption process and Granulated Activated Carbon (GAC) filters cannot be regenerated by backwashing, instead it shall be re-activated typically by thermal process. Depending on the size of the treatment plant, batch vessels can be used to store the GAC beds.

There are recommended at least 2 GAC filters or batch vessels operated in series to prevent breakthrough of contaminants. The carbon filters should be sized to allow sufficient contact time between the effluent and the activated carbon. In general, for the removal of organic contaminants, sizing of GACs is site specific based on the type and mass flow of contaminants to be removed..

3.2.5 SEQUENCING BATCH REACTOR (SBR)

SBR is a fill and draw activated sludge system for wastewater treatment within the same reactor. This technology is typically used when real estate is limited. SBR operations cycle occurs within the same reactor in the following phases: fill, react, settle, decant, and idle.

3.2.6 NANOFILTRATION

Nanofiltration (NF) refers to a specialty-membrane process that rejects dissolved solutes in the approximate size range of 1 nanometre (10 Angstroms) — hence the term “nanofiltration.”
With respect to the size and weight of solutes that nanofiltration membranes reject, NF operates in the realm between reverse osmosis (RO) and ultrafiltration (UF): Organic molecules with molecular weights greater than 200 – 400 are rejected. Nanofiltration membranes can effectively reject large organic molecules.

3.2.7 EVAPORATION

A wastewater evaporator separates water from waste material. Thermodynamic wastewater evaporation involves vacuum evaporation or heating the waste material sufficiently to turn water into a vapor. Several types of evaporators are available commercially, some of which can recover the latent heat of the evaporated water. A key selection factor is the energy consumption that will affect the operational cost. Evaporators must be able to treat a wide range of waste streams simultaneously.

Wastewater evaporation technology is an option for manufacturing processes that generate industrial wastewaters that are hard or expensive to be treated by the conventional technologies or also when “zero discharge” is required. Evaporators can also be used to reduce volume of streams that are hard to treat and consequently reduce incineration costs of remaining solid waste.

3.2.8 ADVANCED OXIDATION PROCESSES (AOP)

AOP, as well as other wet oxidation processes, are aqueous phase oxidation methods consisting of highly reactive species used in the oxidative destruction of target pollutants. AOP creates a more powerful and less selective secondary oxidant, hydroxyl radicals, in the water. The hydroxyl radical has a much higher oxidation potential than ozone or hydrogen peroxide and usually reacts at least one million times faster, thus leading to a smaller contact time and footprint. Despite this secondary oxidant can cause the oxidation of most organic compounds until they are fully mineralized as carbon dioxide and water, we can also use it to break complex molecules into smaller compounds and improve their biodegradability and increase efficacy of the subsequent biological systems.

AOP can combine with ozone, hydrogen peroxide, catalyst, or ultraviolet (UV) irradiation to offer a powerful treatment of wastewater.

Segregating problematic wastewater streams

Always when identifying a wastewater stream that represent a problem to be treated in the available process, we must segregate and evaluate the best approach between establishing a specific pre-treatment or, when this is not possible, needing to find an alternative, for instance treatment in an effective effluent treatment plant offsite or, eventually, the disposal as a hazardous waste through high temperature incineration.

Regardless the approach, the recommendations presented in this Guidance should be followed.

4 WASTEWATER DISCHARGE AND MONITORING

4.1 TYPES OF WASTEWATER DISCHARGES

The typical types of wastewater discharges (treated or no treated) are:

- Direct discharge to surface water, such as rivers, sea, lakes, etc.
- Direct discharge to ground or land that could comingle with groundwater, and eventually with surface water.
- Indirect discharge to surface waters through a third-party treatment facility before getting discharge to the environment, typically to surface water.

Some factors to take in consideration when determining the type of wastewater discharge are the nearby receiving receptors available to the facility such as surface water body and/or third-party treatment facility, the already existing background polluting conditions of the receiving water body which may drive very low discharge limits, and no pre-treatment or treatment technology commercially available to comply with required operational and/or discharge limits. It is important to evaluate how much and what type of treatment is needed based on the characteristics of the wastewater streams (see Section 3. Wastewater Treatment) and the required discharge limits (see Section 4.2. Discharge Compliance Criteria).

Wastewater discharges must meet all applicable discharge limits for the parameters of concern (see Section 4.2. Discharge Compliance Criteria). For the purpose of ensuring compliance with these parameters, wastewater should be monitored before discharging as per permit, agreement, or internal standard requirements, and at different points during the treatment process, for internal controls.

4.2 DISCHARGE COMPLIANCE CRITERIA

Generally, discharge of industrial wastewater requires environmental risk assessments. Appropriate controls need to be implemented and precautions taken not to harm people and the environment and thus protect the companies' reputation and licence-to-operate.

Compliance with laws, regulations and environmental permits is a mandatory requirement. This includes agreements with third party wastewater treatment plants to ensure that the treated wastewater complies with quality standards. If applicable, further regulations must be considered for the receiving water body (e.g., World Health Organization (WHO) Guidelines for Drinking-Water Quality) and other environmental compartments.

Additionally, companies should set internal standards if regulatory discharge limits are not available or not sufficiently protective (as for many individual substances that are not covered by permits). A pragmatic approach is to calculate the Risk Characterization Ratio *RCR =PEC⁄PNEC*, with the Predicted Environmental Concentration *PEC* and the Predicted No Effect Concentration *PNEC* [4, 5].

- *PECs* can be derived from mass-balancing or representative sample analysis. Aspects to consider include
  - Proper sampling (location and timing),
  - Proper analytical procedures with sufficient sensitivity,
  - Removal efficiencies of treatment steps (if downstream of the sampling point), and
  - Relevant equalization in the wastewater treatment plant and the receiving water body.
- *PNECs* should be based on ecotoxicological endpoints for freshwater and/or marine water organisms and appropriate assessment factors, as described for example in [5]. Relevant data can be found by internet research, including sources like e.g.
  - Product registration dossiers published by registration agencies such as U.S. Environmental Protection Agency (EPA), European Food Safety Authority (EFSA), European Chemicals Agency (ECHA),
  - Databases maintained by registration agencies and other national and international organizations, such as World Health Organization (WHO), French National Institute for Industrial Environment and Risks (Ineris), German Environment Agency (UBA),
  - Safety datasheets,
  - International guidelines,
  - Regulations in other countries, and
  - Environmental Quality Standards (EQS).

In line with the ECHA guideline [6], "risks may be considered to be adequately controlled if the Risk Characterization Ratios (RCRs) for each protection target are below 1". Freshwater or marine water organisms are typically the most relevant protection targets for wastewater discharge.

4.3 WASTEWATER DISCHARGE MONITORING

4.3.1 KEY PRINCIPLES OF WASTEWATER DISCHARGE MONITORING

The facility should identify the parameters required to be monitored for compliance and/or operational control, determine representative sampling location(s), decide on the best sampling type and frequency, select the appropriate instrumentation and equipment, establish a calibration and maintenance program, use appropriate analytical methods, and follow laboratory requirements.

Some of the typical parameters that need to be monitored are pH, temperature, alkalinity, hardness, turbidity, Total Suspended Solids (TSS), Dissolved Metals, Salinity/Total Dissolved Solids (TDS), Toxicity, Active Ingredients, Substances of Very High Concern (SVHC), per-and polyfluoroalkyl substances (PFAS), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), and Total Organic Carbon (TOC).

4.3.2 TYPICAL MONITORING STRATEGIES

Typical monitoring strategies consider internal sampling for operational control purposes, and sampling at the point of discharge to prove compliance with permit limits and requirements. Monitoring strategies should be representative of the operation generating the wastewater streams to determine the type, frequency, and location of the sampling of the parameters of concern. For operational control, typically contributing wastewater streams to the wastewater discharge are identified to determine when and where they need to be controlled to avoid impact to the wastewater treatment and discharge characteristics.

4.3.3 MONITORING STRATEGIES

Monitoring frequency depends on how and when contributing wastewater streams are generated to be able to control them before getting discharged. For example, if the wastewater stream is generated in batches, then the monitoring strategy should be to monitor during the period of time representative to the operation. Monitoring frequency for operational control will either depend on how often wastewater characteristics are expected to change, how fast it can be controlled, and economic feasibility. Monitoring frequency for compliance purposes will be determined by the permit or agreement requirements.

4.3.4 SAMPLING AND MONITORING METHODS

Monitoring can be done continuously using in-line instruments or by taking samples at specific locations to be measured by local instrumentation or analysed in the laboratory. Samples can be grab or composite depending on what better represents the impact from the operation or on permit requirements. In-line instruments and laboratory instruments will need to be properly maintained and calibrated as per manufacturer recommendations. When taking samples to be analysed in the laboratory, the facility should take in consideration the use of analytical methods approved by the regulatory agency. Analytical laboratories can be internal or external depending on the resources and facilities available, and it may need to comply with required laboratory certification(s). Monitoring for compliance with permit or agreement should take in consideration requirements related to sample type, sampling location, sampling frequency, and reporting.

4.4 DISCHARGE STRATEGIES

Wastewater can be discharged in batch/intermittent flow or continuous flow. On batch or intermittent flow, the wastewater is held to be tested for the parameters of concern to ensure compliance with the discharge criteria (permit or agreement limits) before releasing it. On continuous flow, the wastewater is getting continuously discharged while getting tested for the parameters of concern, and compliance with the discharge criteria (permit or agreement limits) will be known after discharge has happened. Operational and/or treatment adjustments may be needed to keep the parameters of concern in compliance, and external and internal reporting may be required. During events when the wastewater does not comply with the discharge criteria, diversion structures (temporary or permanent) are used to separate all or part of the flow to a location where it will be stored until it is suitable for discharge.

Sometimes the wastewater discharge limits take in consideration equalization effect from the receiving water body, and a device such as a diffuser can help the fast equalization of the wastewater discharge. A diffuser is a device with multiple ports designed to discharge wastewater into a surface water body.

5 SUMMARY

Proper management and treatment of wastewater is highly relevant for the crop protection industry to prevent environmental damages and reputational risks. This technical guidance document gives a brief overview of management concepts, treatment technologies and discharge criteria for aqueous emissions from production facilities in the crop protection industry.

Wastewater management typically starts with the collection of the relevant data on wastewater streams (flow rates, frequencies, composition, sources) as well as their evaluation as part of Environmental Impact Assessment (EIA) and Environmental Risk Assessment (ERA). Environmental impacts should be reduced by following the wastewater hierarchy of controls, a ranking of suitable control measures starting with the most preferred and effective options, i.e. waste prevention, followed by re-using, recycling, recovering and/or treating and finally discharging. Discharge of wastewater requires a Wastewater Risk Assessment and, if needed, a suitable Wastewater Management Strategy together with an Implementation Management Program.

The design of wastewater treatment processes often requires a smart combination of treatment steps. The selection/combination should be based on (preliminary) treatability tests of single or combined wastewater streams. This document gives a brief introduction into the most relevant processes used in wastewater treatment, including typical application areas, advantages, and weaknesses.

For different types of Wastewater Discharge (to surface water, oceans, ground, and publicly owned treatment works), the site must always fulfil regulatory discharge compliance criteria, and should also set voluntary internal discharge limits to prevent environmental and reputational risks. Finally, the technical guidance document advises on wastewater discharge monitoring. Wastewater discharge monitoring is used to ensure compliance with wastewater discharge criteria.

6 GLOSSARY / DEFINITIONS

Abbreviation	Term	Definition
BOD	Biochemical Oxygen Demand	Oxidation of organic material to Carbon Monoxide and Water by microorganisms at the molecular level. Therefore, oxygen use is an indication of the organic waste content [3].
COD	Chemical Oxygen Demand	A measure of a maximum oxidable substance (unlike biochemical oxygen demand, which is a measure of oxygen removed only by biological organisms). Therefore, COD is a good measure of total effluent strength [3].
	Composite Sample	A sample that consists of multiple grab samples taken over a specific period of time.
	Diffuser	a linear structure consisting of one or more closely spaced ports or nozzles which inject a series of turbulent jets at high velocity into the ambient receiving water body.
	Grab Sample	A sample that consists of a single sample taken at a specific time.
	Hazard	Something that can cause harm e.g. damage to the environment. A hazard can be an object, a property of a substance (e.g. toxicity or flammability), a condition or an activity.
	Hazardous Material	A material that can harm people or the environment due to properties such as toxicity, flammability, eco-toxicity or corrosiveness. Hazardous materials include hazardous substances.
	Hazardous Substance	A form of matter that has uniform composition that can harm people or the environment. Substances are the building blocks of materials.
IBC	Intermediate Bulk Container	A pallet-mounted, plastic container housed in a galvanized steel cage for the transport and storage of bulk liquids and granulated substances. Also known as a tote or pallet tank. IBCs are sized between drums and tanks: most commonly 1000 litres (275 US Gallons), but other sizes such as 1250 litres and 600 litres are also available.
	Mixing Zone	Defined portion of a waterbody where a permitted wastewater discharge undergoes initial dilution.
PEC	Predicted Environmental Concentration	A substance's concentration that can be expected in a certain environmental compartment, such as the receiving water body.
PNEC	Predicted No Effect Concentration	A substance's concentration below which adverse effects are not expected in a certain environmental compartment. PNECs are mostly calculated from ecotoxicological endpoints for relevant organisms.
	Primary Containment	Equipment and infrastructure designed to store or hold materials during normal use e.g. tanks, drums, mixing vessels.
	Risk	The combination of severity of an incident and the probability / frequency of it occurring with that severity.
RCR	Risk Characterization Ratio	Dimensionless number that characterized the relevance of on environmental risk, calculated as the PEC-to-PNEC-ratio.

	Sanitary Wastewater	Wastewater generated by sanitation and related "domestic" activities.
	Stormwater	Water generated from rainfall events or melting snow / ice. It can run-off into surface waters, infiltrate into the ground or remain on the ground surface until it evaporates.
TDS	Total Dissolved Solids	These solids are in solution and pass through the pores of the standard glass-fiber filter [3].
TOC	Total Organic Carbon	The concentration of organic carbon present in a material that is commonly used a simple, non-specific indicator of water or wastewater quality.
TSS	Total Suspended Solids	The material retained on a standard glass-fiber filter disk [3].
	Wastewater	Water that must be discharged or disposed of because it is unwanted or cannot be used due to adverse quality. Wastewater can originate from domestic, industrial, commercial or agricultural activities, or from runoff of rainwater.
WWTP	Wastewater Treatment Plant	Equipment or infrastructure designed to treat wastewater by removal of physical, biological and/or chemical contaminants. Also known as an "Effluent Treatment Plant" (ETP).

7 REFERENCES

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