Whole Effluent Assessment (WEA)

A new approach to assessment and control of water quality

Introduction

Refineries handle significant volumes of water, often comparable to the amount of hydrocarbons they process. In common with many industries some of this is discharged as an effluent. Traditionally most effluent discharges have been assessed and controlled using physical and chemical properties such as pH, temperature, chemical oxygen demand and concentrations of specific components such as oil or heavy metals. This type of approach has been successful in reducing the discharge of hazardous substances and has contributed to the substantial improvements in water quality across Europe. It is particularly suited to relatively simple effluents, especially where the discharged substances have known properties, e.g. the likelihood to cause ecotoxicological impact. As the quality of receiving waters in Europe has improved attention has increasingly turned to more subtle effects. Ultimately the aim of improving discharge water quality is to improve the condition of the receiving water, thus minimising risks to both human health and the state of the ecology. Focus has therefore shifted from the physical and chemical characterisation of water quality to its biological quality. Such biological effects measures encompass a broad spectrum from specific toxicity studies on an effluent (either before or after discharge) to monitoring the health of the ecosystem within a receiving water body such as a river or a lake. Such techniques have been used in a limited way in some European countries for many years. They are now starting to enter the mainstream of European regulatory control and are already being used by some companies to assess their own discharges and impacts.

At first glance, the use of such biological effects measures appears a logical step. Tests based upon biological impacts relevant to the ecosystem to be protected appear to make sense. However, finding out what is 'relevant' in this context is not straightforward. Many tests have been developed for use on specific chemicals rather than with a whole ecosystem in mind. Not all of these tests provide an indication of impact upon the 'real' environment. The complex interplay of stresses on the ecosystem makes it very difficult in practice to demonstrate cause and effect relationships. All of this requires a substantial amount of expert judgement to be applied when interpreting data, and a regulatory regime that allows for this flexibility.

In an earlier CONCAWE *Review* article (Vol. 10 No. 2, October 2001) we looked at the state of development of WEA as it was then. This update highlights increased confidence in the application of this methodology.

What is WEA?

The terminology in this area is sometimes confusing as identical terms are used for different things! Whole Effluent Assessment (WEA) refers to a suite of tests used to characterise the quality of an effluent before, during and after discharge. In its broadest sense WEA includes chemical, physical and biological measures, but it is not uncommon to use the term solely to refer to the biological assessments. In this article the biological aspects of WEA will be discussed as these are less familiar to most people, but the reader should remember that classic chemical and physical tests will often complement the biological steps.

The major biological components of WEA cover the three parts of the commonly used acronym PBT—namely Persistence, (potential to) Bioaccumulate, Toxicity. More recently other attributes such as Mutagenicity and Endocrine Effects have also been included in some WEA approaches. Each of these is discussed below.

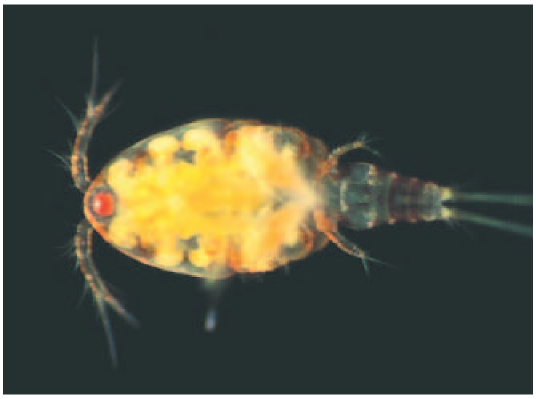
Toxicity

The most commonly used tests in a WEA scheme are those used to assess toxicity. These are probably the best understood tests and many schemes start with some form of toxicity assessment as a first screen. WEA has relied upon methods developed for hazard assessment of single substances. Their use in WEA demands that other factors, including varying composition of effluents with time, interactions within complex mixtures, actual test conditions leading to changes in sample composition and temperature effects be considered. Nevertheless such tests can be used effectively with suitable modifications.

There are two main types of toxicity—acute and chronic toxicity. Acute toxicity is defined as the adverse effects of a sample on an organism or surrogate, exhibited within a short period of exposure. Typically the term 'short' is taken to mean up to 12 hours for a single celled organism and up to one third of the time taken from birth to sexual maturity for invertebrates. This could equate to a period of 2–4 days for higher organisms. Acute toxicity is usually assessed as lethality or immobility (fish and invertebrates) or reduced growth or metabolic function (algae and bacteria). Chronic toxicity is defined as the adverse effects of a sample on an organism or a surrogate, exhibited after a long time period in relation to the lifetime of the organism. Chronic toxicity is usually measured by assessment of sub-lethal effects, e.g. reduced growth rates.

The objective of acute toxicity evaluation is to identify emissions which have immediate toxic effects in the environment and are usually directed towards a point of discharge, although the evaluation can also be carried out on the receiving water. They are generally well understood tests, are relatively cheap and quick to perform and so are the most common form of testing employed. The objective of chronic toxicity tests is to identify discharges which have a detrimental effect over longer time periods. Because of their higher costs and longer timescale they are carried out less frequently. In many cases this will be after an acute toxicity testing regime has already been carried out as part of a stepwise approach to achieving environmental improvements.

A variety of standard test methods are available for both acute and chronic toxicity testing. It is outside the scope of this article to review these in any detail. Commonly



Tisbe—*a typical crustacean used for acute toxicity testing*

used acute tests applicable to WEA include algal growth inhibition, daphnid tests, bivalve embryo larval development, crustacean mobility and fish tests. Chronic toxicity tests use similar species with longer exposure times and non-lethal endpoints. There are a number of limitations and interferences with these tests (as with all analytical methods) and the data require careful interpretation. Assessments can be carried out in a variety of ways—as static, flow through or even as *in-situ* tests. Each method has a specific range of applicability and again expert judgement is required to select the most appropriate, depending on the goal of the testing. Traditionally, effluent toxicity assessments would be carried out using tests across three trophic levels of organism, i.e. bacteria/algae, invertebrates and fish. The use of fish testing is subject to various ethical and cost concerns and its use has been much reduced in recent years. Alternatives such as fish egg development, fish cell lines and the use of solid phase micro-extraction (SPME) techniques have been evaluated. So far no particular technique has emerged as a direct replacement and work continues.

As well as traditional tests using conventional organisms, a variety of methods is being developed to speed up and simplify assessment procedures. Microbiotests are one such approach and examples include Toxkits™, CerioFAST™, and Microtox™ all of which have been used for WEA applications. They may have the advantages of speed and the requirement for less specialised staff to carry out the testing. Nevertheless, their ecological relevance is less obvious and they often do not have

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The use of in vivo *fish testing has been much reduced in recent years for ethical and cost reasons.*

regulatory acceptance. They can be of benefit in internal investigations where their speed can allow a lot of data to be gathered rapidly. Calibration against more conventional test data can help to identify the ecological relevance for a particular site or discharge.

Bioaccumulation

Bioaccumulation of substances is of significant concern as it can lead to the exhibition of toxicity at different levels in the food chain. Typically, substances for which bioaccumulation may be an issue have octanol-water partition coefficients (log K_{ow} values)[1] between 4 and 7, have sufficiently long residence times in contact with the organism to be able to partition to it and are metabolised only slowly (or not at all) by the organism. Many hydrocarbon chemicals have log k_{ow} values in the range where bioaccumulation is possible.

Testing of bioaccumulation potential is usually based upon physico-chemical characteristics of substances and so can only indicate the potential to bioaccumulate. Data generated by such methods can only be used to screen samples for possible impacts. The potential to bioaccumulate is a questionable concept when applied to effluents. It is perhaps more accurate to state that certain components of an effluent, rather than the effluent itself, have the potential to bioaccumulate. A number of surrogate tests have been developed to assess this potential. The most common are High Pressure Liquid Chromatography (HPLC), Solid Phase Micro-extraction (SPME) fibres and the Empore (C18) discs test. Exposure times vary considerably (1 to 20 days) making comparison of data very difficult. At present, the only way to assess actual bioaccumulation with certainty is to measure the component(s) in an organism after a period of exposure. This is time-consuming, requires specialist staff and a dead organism. Establishing the level of component in the organism before exposure can present a challenge to scientific rigour.

Persistence

Persistence is of regulatory interest because, in principle, the longer an organism is in contact with something, the greater the potential for an adverse effect to occur. This of course presupposes an adverse effect can occur. Persistence can be defined in terms of the resistance of a substance to degradation in the environment by processes such as biodegradation, hydrolysis or photolysis. Persistence is something of a negative determinant—it is not measured directly but interpreted from the continued presence of something. Normally persistence is measured as a degradation half life and values in excess of 50 days are usually taken to mean something is persistent. It is less easy to apply the term persistent to effluents which are often mixtures of components. None of the standard tests for determination of persistence (usually biodegradation tests) have been designed to assess the persistence of mixtures and all have limitations for this purpose.

It is perhaps more relevant in the context of effluents and WEA to talk about the persistence of a property such as toxicity or bioaccumulation potential. This approach can help to identify areas of concern which require further evaluation. The use of assessment schemes combining biodegradation tests with the evaluation of toxicity or potential to bioaccumulate both before and after biodegradation, have proved valuable. Many materials are persistent—this does not automatically mean they are harmful.

Endocrine disruption, mutagenicity and genotoxicity

Endocrine-disrupting chemicals have been described as 'exogenous agents that interfere with the production, release, transport, metabolism, binding and action or

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[1] *Common measure of fraction which partitions to either the water or oil phase, used here to indicate the partitioning to fat tissues in the body of an organism*

elimination of the natural hormones in the body responsible for the maintenance of homeostasis and regulation of the developmental process' (Kavlock *et al.* 1996). This area has attracted substantial regulatory interest, as there is concern that the more traditional methods described above may fail to predict chronic reproductive and development impacts caused by this mode of action. To date no regulatory controls have been imposed. The test methods used are time-consuming, complex, expensive and open to considerable debate as to their environmental relevance. Their use in WEA approaches is unlikely at present, but they are the subject of extensive development work.

Mutagenicity is a term used to describe the ability to cause permanent transmissible changes to the genetic material of cells or organisms. It is used to a limited extent in an effluent regulatory context, although the tests involved are single-substance tests. The applicability of these tests to effluents and their ecological relevance is still unclear. Tests are divided into two main types—bacterial tests such as the Ames assay and eucaryotic tests which use microscopic analysis of genetic material after suitable highlight treatment such as staining.

Genotoxicity is a term used to describe non-transmissible changes in genetic material. It is not explicitly used in a regulatory context. Test methods are similar in nature to those for mutagenicity and include the umuC assay and the Comet assay. The environmental relevance of such tests is unclear and so it is not easy to pinpoint appropriate actions to control this phenomenon.

It is generally true to say that toxicity (both acute, and to a lesser extent chronic) is the only well understood and applied criterion for WEA use so far. The use of persistence and the potential to bioaccumulate in appropriate assessment schemes is becoming more widespread but interpretation of data requires expert judgement. Mutagenicity is applied in a limited regulatory framework but its environmental relevance is not clear in the context of effluents. Other approaches described above do not yet appear ready for widespread deployment and considerable work is still required. Nevertheless, it must be recognised that these approaches are raising a whole set of new questions about discharge and water quality. The risks associated with this and the preventative measures necessary to minimise or eliminate these risks must be evaluated.

Why might WEA matter to a refinery?

Many people in the refinery business will assume their effluents to be much less complex than, for example, a chemical manufacturer's, and so question what WEA means to them. The reality is that refinery effluents have the potential to contain a very complex mixture of organic and inorganic chemicals with varying ecological impacts. As well as the many hydrocarbons and other components of 'oil', refineries also handle and process a wide range of other chemicals from catalysts to corrosion inhibitors, all of which have the potential to be measured in some way in WEA tests. With much work already done to reduce the impact of discharges, it makes sense to target any further efforts towards the discharges or parts of a discharge with the most potential impact on the receiving water. The use of WEA could help to provide this focus. Additionally the use of WEA approaches can help to demonstrate the absence of risk of harm from a discharge.

WEA is increasingly being applied in regulation. The IPPC BREFs for Waste Water, Waste Gas and Economics and Cross Media Issues (in draft) already contain references to WEA methods as a means to assess and demonstrate BAT[2].

Refinery effluents may contain a very complex mixture of organic and inorganic compounds

[2] *Best Available Techniques*

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Several European countries (e.g. Germany, Ireland, UK, Sweden) already use some aspects of WEA in their regulatory regimes and many others are developing such approaches (see Table 1). It is possible that WEA approaches could be used as a tool to support the assessment of Good Ecological Status as required in the Water Framework Directive. OSPAR[3] is studying the use of WEA as a means to reduce or eliminate the presence of Priority Substances from the marine environment. Virtually all refineries are likely to encounter one or more of these regulatory issues.

As the focus moves towards controlling an increasing number of hazardous chemicals, it could prove cost-effective to focus instead on using WEA tools in a risk assessment process to achieve the same goals. Additionally, WEA tools can be used to assess effluent streams within a refinery to identify problematic streams and target them for management at source. This approach can also be beneficial in handling effluent treatment plant problems by identifying which streams are affecting the biology within a treatment plant itself.

Table 1 Some examples of regulatory approaches of WEA *(after Power & Boumfrey, 2003)*

Country	Outline of WEA scheme
EU Generic	IPPC Directive 96/61/EC BAT and related to Environmental Quality Standards. Water Framework Directive good water quality objectives may use a Whole Effluent Toxicity approach.
Belgium	EU approach with sector-specific conditions based on BAT. Demonstration programme being used to develop protocol.
Denmark	Non-statutory approach including biodegradation and bioaccumulation. Source control used to protect receiving water.
Eire	Mandatory Emission Limit Values based on toxic units. Source control primary vehicle with some receiving water monitoring.
England, Scotland and Wales	Small number of consents in place. Direct Toxicity Assessment demonstration programme (industry and regulator initiative) developed protocol for acute toxicity testing. Bioassay use expected to increase where receiving water quality is assessed as poor.
France	EU & routine monitoring. Some site-specific licensing. Used as basis for taxation.
Germany	Regulatory use as hazard reduction under wastewater ordinance and wastewater charges act. Basis of taxation. Primarily source control but also uses daphnids for early warning in large rivers. Some states assess mutagenicity and endocrine effects.
The Netherlands	EU and risk-based approach to account for receiving water conditions. May be used for source control following evaluations.
Norway	Can be applied as regulatory instrument. Emission Limit Values and site specific limits. Source control based upon total emission factors.
Spain	Regional use in permits. Source Emission Limit Values. Hazard based source control. Some taxation of discharges.
Sweden	Surface water protection is main goal. Bioassays used to license some discharges. Source control can include biodegradation and bioaccumulation.
OSPAR	Intersessional Expert Group developing methodology in context of OSPAR Hazardous Substance elimination goals. Currently expected to include assessment of Persistence, Bioaccumulation & Toxicity but details still under development.

[3] *Commission for the Protection of the Marine Environment of the North-East Atlantic (previously 'Oslo and Paris Commission')*

What's happening?

As outlined above, WEA concepts in regulation are being applied to an increasing degree within several countries. CONCAWE's Water Quality Management Group is starting a new Task Force to look at a range of biological effects measures including WEA. One of the aims of this task force is to collect data from operators on the application of WEA assessments at their sites. The intention is to identify the issues and risks involved, and potential benefits coming from their use. A further area of study is to understand the ecological impact of operational changes both in processing and water treatment facilities. Process changes to reduce emissions or optimise performance can have unanticipated effects that WEA techniques can help to identify. This process is already widely used in the chemical industry. As data is gathered this will be developed into a good practice guide to support refineries as the use of this approach increases.

OSPAR is one of the primary legislative drivers for WEA. CONCAWE has a seat on the OSPAR Intersessional Expert Group for WEA and is actively participating in this joint regulator/industry group, bringing expert technical knowledge of the application of WEA methods in the oil industry. Such contributions have significantly influenced the direction of the OSPAR work and have allowed a realistic consideration of a risk assessment approach to be retained within OSPAR's hazard identification framework. CONCAWE is also contributing to an ECETOC task force producing a report on industry experience with WEA. The report includes recommendations for methodologies which can be used to apply WEA methods in practice and these will be discussed at an industry sponsored workshop to be held early in 2004 with OSPAR. These activities will also contribute to the debate on the efficacy of WEA methods and their application in practice to gain environmental improvement. Both of these activities have brought about recognition of the level of expertise available within the industry, thus enabling our views to be taken seriously in the debate. OSPAR is increasingly moving towards assessment of the environment to evaluate the effect of its measures to eliminate harmful discharges. WEA is consistent with this approach and is likely in due course to find a wider role within OSPAR.

In European legislation WEA (in the form of toxicity assessment) is already mentioned in the context of BAT development under IPPC. The concepts also have potential for application within the Water Framework Directive to assess ecological water status. At present this application is regarded as only a possibility but the activity is being tracked. Again the EU Commission is starting to look more at the health of the environment rather than at specific substance controls, and developments are likely to continue.

The use of WEA-type approaches raises new questions about the impact of discharges, emissions and losses from sites. These questions may pose different risks to our operations and to the environment. The new CONCAWE Task Force specifically aims to understand this new area and to identify the optimum way forward.