An Approach Integrating Chemistry and Toxicity for Monitoring the Offshore Platform Impacts

L. Manfra and C. Maggi
ISPRA Italian Institute for Environmental Protection and Research, Rome, Italy

1. Introduction

The world natural gas production grew substantially in 2010, by more than 6% (3275 billion cubic meters), the highest rise among fossil fuels and the strongest increase since 1994. (Enerdata, 2011). The gas production in European countries grew 3% in 2010 (314 billion cubic meters, with 8 billion cubic meters produced in Italy) (Assomineraria, 2011; Enerdata, 2011). More than 100 offshore gas platforms have been deployed since the 1960s in the northern and central parts of the Adriatic continental shelf, representing the highest concentration of fossil fuel extraction platforms in the Mediterranean area (Manoukian et al., 2010).

The offshore platform activities comprise different phases linked to exploitation of gas and oil reservoirs: a) the exploration phase to probe the position and the geological characteristics of well and then to install a steel platform; b) the production phase to extract oil and gas; c) the decommissioning phase, when the commercial life of well is finished (Oil Industry International Exploration & Production Forum/United Nations Environment Programme [E&P Forum/UNEP], 1997).

The environmental impacts linked to exploration and production phases are more remarkable than those related to decommissioning phase as often, when the platform life is ended, the submerged part of structure (the jacket) is left on the seabed avoiding the removal disturbs further the seafloor integrity.

Criteria for environmental monitoring in the vicinity of offshore oil and gas installations are according to international programmes (e.g. OSPAR Convention). The guideline goals are: a) to monitor selected chemical and physical variables of water column and sediment; b) to evaluate effects on biota; c) to identify spatial-temporal trend of the eventual alteration that could occurred. In order to give the best description of the environmental quality status an integrated approach may be applied by means physical analyses, chemical analyses, ecotoxicological assays, bioaccumulation studies, ecological investigations (macrozoobenthic community and fish assemblage studies) and acoustic investigations. The monitoring may be devised as flexible tool allowing modifications when the activities are in progress, if results of previous year activities request it (Trabucco et al., n.d.).

In this paper we would describe a key aspect of monitoring that allows to evaluate the environmental health status, potential load of pollution on environmental matrices and effects on biota due to offshore platform presence: integrated chemical and ecotoxicological approach.

The traditional chemical analyses allow to evaluate the behaviour of some environmental parameters (e.g. dissolved oxygen, chlorophyll, nutrients) and contaminants when a platform is installed and/or in production phase. Chemistry gives information on the presence, quantity and chemical form of substances linked to platform activities.

The integration of biological investigations allows an assessment of toxicity and bioavailability of contaminants, to understand the mechanisms of their toxic action and identification of the area of potential biological impact of platforms and/or their discharges.

The purposes of this paper are to a) provide an overview the main environmental impacts of installation and production activities, b) explain the importance of an integrated chemical and ecotoxicological approach for environmental monitoring plans, in particular for offshore platform monitoring, c) present the results collected, for many years, around several gas platforms located in Adriatic area (Mediterranean Sea).

2. Main environmental impacts of platforms and major production discharge

Environmental impacts may arise at all stages of oil and gas activities, including initial exploration, production and final decommissioning. The main pressures on the marine environment from oil and gas activities include the placement of installations on the seabed and operational and accidental discharges. In addition there could be concerns related to atmospheric emissions, low level naturally occurring radioactive material and noise (Commission protecting and conserving the North-East Atlantic [OSPAR], 2009). Finally, offshore platforms undergo subsidence, especially due to production activities (Setan & Othman, 2006).

The quantification and interpretation of the environmental effects of offshore platforms can be difficult and hard to generalize. Although the physical presence of the structure is a common characteristic to all the platforms, several local abiotic and biotic variables influence the effects of each platform in a unique and different way. The radius of impact can be different depending on the number of platforms placed in a restricted area, the structures' dimensions and biogeographic/climatic factors (Manoukian et al., 2010).

2.1 Impacts related to platform presence on the bottom

The placing a structure on the seabed may cause a physical impact on the seabed, that varies on a case by case basis depending on the particular sensitivities associated in the area. Physical impacts on the sea bottom will occur in connection with installing pipelines, cables, bottom rigs, templates, skids, and platforms including platform legs and anchoring. Due to the number and length of pipelines placed on or under the seabed the overall physical impact of pipelines is greater than those from the other installations or operations mentioned above (OSPAR, 2009).

First, the physical structure of the platform may determine some alterations in the environment: changes in local water flow, in the rate of erosion or sedimentation, modification in bottom morphology, variation in grain size and organic content in sediments, and then in the number of predators present.

Second, offshore platforms may cause disturbance of the seabed and mobilisation of sediment. The volume and distance that suspended sediments disperse depends on particle size, weight and current velocity. However, it is possible that the positioning of the structure results in a temporary increase in turbidity due to the material raised from the bottom. Third, the use of antifouling paints to combat bio-fouling and the use of corrosion protection systems (anodes) containing metals (e.g. Zn, Al and Cd) can lead to contamination phenomena in water, sediment and biota. Although there is a ban on using antifouling paints containing organotin compounds, their persistence is such that even today these compounds are found in sediments and tissues of organisms living in the vicinity of the platforms.

Fourth, physical structure may cause biotic modifications, affecting the benthic community composition and the responses of organisms exposed to eventual contaminations linked to installation phase. The scale of the impact also depends on the vulnerability of benthic communities in question, as well as the distance from the platform itself and the time elapsed since its installation (Trabucco et al., 2006). Historical monitoring has demonstrated that the impacts are largely transient, with re-colonisation of disturbed seabed habitats occurring within relatively short timescales. The creation of hard bottom substrate can, over time, give an opportunity for new benthic species to colonise the former sandy/mudflat areas. Pipelines, platform legs and subsea templates may act as shelter for fish and other mobile marine organisms, and provide a habitat for benthic organisms usually associated with hard substrates (OSPAR, 2009). Some studies highlighted the effects of platforms on benthic communities over the time. In most of these cases, the more relevant ecological alteration due to the presence of a gas platform was a mussel mound development affecting the surrounding seabed communities within a radius of a few meters (Manoukian et al., 2010 and references therein).

2.2 Impacts related to main waste fluid discharged from platforms

In the offshore oil and gas industry, produced water constitutes the main source of oil input in marine water basin. It is the principal aqueous waste resulting from production operations. It originates from water naturally present in geological formations (formation water) and water injected in the oil field (process water) to maintain reservoir pressure. Its disposal is carried out through the reinjection into the reservoir, the discharge into the ocean or the transport onshore. After the release into the sea, the produced water undergoes several different processes such as the dilution into the ambient fluid (which may occur more or less rapidly depending on local oceanographic conditions), the evaporation and biodegradation (that change the concentration and composition), the volatilization towards the atmosphere and the settling at the bottom (Stromgren et al., 1995 and references therein).

The environmental impact of this effluent is a function of (a) the loading and type of the contaminants present in produced water, (b) the partitioning of the chemical constituents in the environment, and (c) the nature of the receiving environment and its dispersion characteristics (Rabalais et al. 1992; E&P Forum/UNEP, 1997). Generally, the presence and, consequently, the effects of produced water substances on biota are dependent on a number of factors: bioavailability, bioaccumulation, biomagnification, toxicity and the capability of the organism to metabolise the substance. The bioavailability of the substance is dependent on the chemical form (speciation) in which it occurs. Rarely contaminants may occur in the water column or in solution. Many of the contaminants of concern in the marine environment have low water solubility and a high affinity for particles. In fact, some substances tend to adsorb on suspended solids both within produced water and in the water column; in this way, they can reach the seafloor and once there they may become incorporated in seabed sediments and become potentially available to filter feeders. Contaminants can be taken up by organisms either directly, by absorption from sea water, or by ingestion of particles and can be relayed to successively higher levels in the food chain via grazing and predation (OSPAR, 2009).

So on, the characteristics of some typical constituents of produced water (e.g. organic compounds, inorganic compounds and chemicals) and then their fate and effects are briefly described. Produced water contains organic compounds such as dispersed oil (in droplet form), dissolved oil, organic acids and phenols. In particular, volatile aromatic compounds as Benzene, Toluene, Ethylbenzene, Xylenes (BTEX) and low molecular weight aromatic hydrocarbons as Naphthalene, Phenanthrene and Dibenzothiophene and their alkyl homologues (NDP) are mainly in dissolved form, while high molecular weight Polycyclic Aromatic Hydrocarbons (PAHs) are present as dispersed oil. These compounds may be removed from seawater by means of volatilisation, adsorption to particles, sedimentation, biodegradation and photolysis. Many organic compounds interact whit suspended material and the particulate matter could affect their mobility. Exposure to marine organisms is low and may cause narcosis, alterations of permeability of cell membranes and developmental defects. PAHs are relatively insoluble and their potential for bioaccumulation increases with increasing molecular weight. They may be toxic in different way as narcosis, phototoxicity, biochemical activation, etc. Phenols are soluble in marine waters, highly volatile and degradable; they appear not particularly toxic to aquatic organisms (Cianelli et al., 2011 and references therein). Produced water also includes inorganic compounds as chlorinates, carbonates, sulphurs, sodium, potassium, calcium, ammonium and trace metals (copper, nickel, iron, chromium, manganese, lead, zinc, barium, arsenic, mercury and cadmium). Many important trace elements are transported through aquatic system as colloidal chemical compounds or are sorbed to solid particles. The chemical form of the metals depends upon pE: ions held by cation-exchanging clays, bound to hydrated oxides of iron and manganese or chelated by insoluble humic substances (Mansour, 1993). The most common trace elements in produced water are barium, iron, manganese, zinc and lead; co-precipitation reactions and adsorpion process favour partition of these metals on solid phases (Scott et al., 2007). Although less available than ones in solution, metals absorbed on small particles are more accessible than those in sediments. Among the factors involved in metal availability are the identity of the metal, its chemical form (type of binding, oxidation state), the nature of suspended matter, the type of organism and the physic-chemical condition of receiving water body. Some of heavy metals are essential at low levels but toxic at higher levels; lead, cadmium and mercury have notable toxicological and environmental significance. The most of heavy metals are particularly toxic in their chemically combined forms, the others, notably mercury, in the elemental forms (Sittig, 1991). Cadmium adversely effects several important enzymes; lead has a number of toxic effects, including inhibition of the synthesis of haemoglobin; arsenic is a metalloid which forms several toxic compounds; elemental mercury penetrates the blood-brain barrier, divalent ionic mercury damages the kidney and organometallic mercury compounds, as metilmercury, are very toxic (Maggi et al., 2009). The toxicity of heavy metals in suspended matter and their availability to organisms are very important in determining the environmental effects in aquatic system.

The reservoir fluids (oil, gas and water) are separated on the platform and chemicals may be added at various stages during this processing to aid oil-water separation and mitigate operational problems. Chemicals may include corrosion inhibitors, demulsiners, defoamers and biocides. Some of these production chemicals are appreciably toxic in standard toxicity tests, although the environmental fate and effects associated with their use will depend on a number of factors. These include: a) the fraction of the chemical released with the discharged water (as opposed to being entrained with the oil), which is determined largely by the oil/water partitioning characteristics; b) the mode of use (continuous low dosing or higher dose batch treatment); c) the chemical injection point within the process system (Henderson et al., 1999 and references therein).

3. Environmental monitoring plans and importance of an integrated chemical and ecotoxicological approach

In general, environmental monitoring programs collect data for one or more of the following purposes:

1. to establish a baseline; that is, gathering information on the basic site characteristics prior to development or to establish current conditions;
2. to establish long term trends in perturbed or unperturbed systems;
3. to estimate inherent variation within the environment, which can be compared with the variation observed in another specific area;
4. to make comparisons between different situations (for example, pre-development and post development; upstream and downstream; at different distances from a source) to detect changes; and
5. to make comparisons against a standard or target level.

What is the role of chemical analysis in evaluating environmental quality? And what the ecotoxicology? Why an integrated approach of these two disciplines is important?

3.1 Chemical analysis and bioassay in environmental quality assessment

The knowledge of chemical analysis today has become important not only for scientists in their research but in fact bears influence in our daily routine as well. Chemical analysis is a vital first step in environmental research. It is a body of procedures and techniques used to identify and quantify the chemical composition of a sample. Qualitative chemical analysis is used to identify a particular element, compound or substance present in a sample while quantitative analysis consists of determining the concentration of these substances. The primary advantage of measuring chemical concentrations in environmental media such as water, soil and biota is that they provide evidence of past or present exposure to environmental pollutants and of speciation. However chemical criteria usually do not include multiple chemical exposures and, for this reason, should be associated to biological investigations.

Biological criteria, on the other hand, are not only reflective of chemical exposure, but have the capacity to integrate many of the physical, chemical, and biological stressors that operate in ecosystems. In addition, many biological criteria are capable of integrating the effects of stressors on organisms both spatially and temporally, and are thus more suited for measuring and interpreting the possible effects of multiple stressors on both terrestrial and aquatic ecosystems (Adams & Tremblay, 2003). Biological tools for environmental assessment may be classified into three groups: 1) exposure and effect biomarkers that measure biological responses in local populations of non-migrating animals, 2) ecotoxicological bioassays that test the toxicity of environmental samples with standard biological models, 3) biological indices that measure diversity and related traits at community level. These three kinds of biological tools show, on one hand, increasing ecological relevance but on the other, decreasing early-warning value. In particular, community indices are not preventive, since effects may only be visible late in time, or may be impractical due to natural variability and cost-effectiveness limitations. Therefore, alternative rapid and sensitive biological tools, such as the effect biomarkers and bioassays developed in the last few years by the International Council for the Exploration of the sea and the Convention for the protection of the marine environment of the Northeast Atlantic, should be implemented (Beiras et al., Personal Communication).

Alterations at the molecular and cellular levels (biomarkers) can provide a sensitive indication of early changes, which often represent the first warning signals of environmental disturbance, even in the absence of acutely toxic responses. A multi-biomarker approach can be used in environmental prognosis to predict long-term toxicological effects or changes in the higher levels of biological organization.

Laboratory bioassays are a common procedure to evaluate toxicological endpoints at organism level, in a large number of test species from across several taxa, and across the main ecological or trophic positions (i.e. from bacteria to fish, and from decomposers to final consumers). (Piva et al., 2011 and references therein). It is very important give a toxicity judgment considering the response of more species. In fact, the differences in intrinsic properties of species determine their sensitivity to various chemicals. If this shape differs for different chemicals and the sensitivity of the various species to these chemicals differs strongly, one can expect, that in a sample (e.g. sediment) with a mixture of various contaminants and bioavailabilities the responses of organisms show very different response patterns, also depending on the endpoint – the physiological reaction that is measured in the test (Ahlf & Heise, 2005).

Environmental quality can no longer be assessed solely on the basis of a more or less comprehensive set of chemical analyses, nor by comparing individual determinations of chemical concentrations against arbitrary standards with no ecological basis. Pollution monitoring, either intended to identify geographical patterns of pollution or temporal trends, must nowadays be based on integrated approaches involving complementary chemical and biological methodologies (Beiras et al., Personal Communication). Toxicity tests permit to evaluate effects of contaminants alone or in mixtures; additionally, they also assess effects of those contaminants that have not been detected chemically (Ahlf & Heise, 2005). The interconnected roles of chemistry and ecotoxicology address questions relating to the presence of chemical pollutants, their bioavailability, and the onset of adverse effects at different levels of biological organization (Chapman, 2007). As example we report in Table 1 the advantages and limitations of chemical and biological criteria in environmental management.

Criteria	Advantages	Limitations
Chemical	• Provide specific chemical concentration • Provide chemical speciation • Well-proven technology • Short-term response • Generally reproducible • Fast turnaround results	• Not provide bioavailability • Not provide synergies • Not ecologically relevant
Biological	• Estimate to contaminant bioavailability • Relate directly to risk • Assess synergic effects • Tests in situ are realistic	• Variability a concern • Some criteria lack validation • Lab tests lack realism

(source: Volpi Ghirardini and Pellegrini, 2001; Adams and Tremblay, 2003)

Table 1. Some advantages and limitations of chemical and biological criteria in environmental management.

3.2 Chemical analysis and bioassay for offshore platform monitoring

A series of chemical and biological analysis tools may be employed to monitor environmental effects when a gas platform is installed and/or a produced water is discharged into the sea. In fact, concerns existed that contaminants associated to offshore activities (installation and/or production phase, with operational or accidental discharges) could be accumulated within sediments and marine organisms and result in significant negative effects on the marine environment.

Accumulation analyses (in sediment and biota), together biomarkers and toxicity tests in situ, may help the scientist to understand what happen to organisms present where there is an platform or a produced water discharge. Besides, laboratory tests may be carried out on species directly exposed to produced water or to environmental matrices, collected in gas platform and/or produced water discharge area.

The integrated chemical and ecotoxicological approach generally provides information on the following aspects in evaluation of potential effects of offshore platforms and produced water discharge:

1. Investigation in environmental media (water, sediment, biota) of contaminants potentially associated to the platform presence (e.g. trace metals as zinc, aluminium, cadmium or barium). In this context, chemical speciation allows to distinguish between

the anthropogenic impact connected with platform activities and the natural regional gradient of contaminant levels in water, sediment and biological tissues.
2. Assessment of toxicity and extent of toxic effects recorded near to platform area. Some chemical compounds used during installation may be dangerous for biota; however it is not always possible to distinguish the contribution of the toxicity caused by installing from that due to production phase.
3. Analysis of chemical composition of produced water and fate of its constituents in marine environment. If the concentration of some substances in environmental sample is found to be significantly higher than the background levels, then the bioavailability and ecotoxicity of these substances on selected species may be further considered.
4. Analysis of some produced water contaminants used as chemical tracers to describe the dispersion of effluent into the sea; in fact, some compounds (salts, nutrients, isotopes, ions) may be used as tracers. A substance may be conveniently used as a tracer if it has some proprieties: conservative, representative of produced water, easy to analyse and to monitor (Cianelli et al., 2008).
5. Bioaccumulation studies to evaluate produced water contaminant concentrations in edible tissue of fish and invertebrates collected near discharge;
6. assessment of short-term and long-term effects of produced water on marine organisms and estimation of potential biological impact area around discharge point. The toxicity studies are used as a complement to chemical measures for quantifying the potential toxic effects, together with the bioavailability of chemical substances and the possible synergies.

Details on chemical analysis, biomarkers and toxicity tests, with reference to sampling operations and laboratory analyses are reported in Trabucco et al. (n.d.).

4. A review of field studies: The Adriatic gas platforms (Mediterranean Sea)

The exploitation of gas fields in the Adriatic sea began in the 1960s and more than 100 platforms have been installed since then, which extract especially gas. These offshore structures are mainly distributed along the Northern and Central Adriatic coasts (about 90 platforms but also in the Ionian Sea and in the Strait of Sicily (De Biasi et al., 2006).

Adriatic is a shallow, landlocked semi-enclosed sea in the eastern Mediterranean, characterised by a wide shelf; with an average depth of few tens of meters in its northernmost section, and less than 200 meters in its middle portion, and a relevant seasonal variability in its circulation dynamics. It is a basin characterized by strong gradients in water properties due to important surface (air sea) and lateral (river runoff) fluxes. In the Adriatic Sea thermohaline stratification and current field may also crucially affect the impact of effluent discharges, such as produced water discharge (Cianelli et al., 2011).

The importance of assessing the impact of offshore activities on the marine environment has been widely recognized using different tools (chemical analysis, physical modelling, biological investigations etc.). In this context, we present results of some studies, carried out in the Adriatic Sea, that have adopted the chemical and ecotoxicological approach, both for monitoring of platforms with produced water discharge and platforms without discharge.

In case of release of produce waters into the sea, it is important consider that the most of Adriatic platforms produce gas and this means a higher content of low molecular-weight aromatic hydrocarbons and small water volumes compared to oil platforms. These may be important elements to take into account when they come to mitigating the impact of discharge.

Mariani et al. (2004) studied produced water collected from an off-shore gas platform located in the Central Adriatic Sea (Italy), including analytical determinations and acute toxicity bioassay by using the European sea bass (*Dicentrarchus labrax*) fish larvae. The chemical characterization, concerning inorganic and organic compounds, was carried out in the liquid phase, and also on the produced water solid fraction. The trace metals were found to be linked only to the solid fraction while the aromatic hydrocarbons and phenols were absent in all the matrices analysed. Examining and comparing the mortality time to unfiltered and to filtered produced water, they observed a shorter response time to the unfiltered sample, probably induced by chemical effect (contaminants associated with particle of produced water) or to particle mechanical effects (i.e. absorption through body surface and gills or oral ingestion/digestion).

Manfra et al. (2007) carried out a chemical and ecotoxicological assessment on the produced water and sediments around a gas platform. The chemical analysis has shown high concentrations of zinc and arsenic in sediment samples only in the nearest station to the platform. Zn was recorded in produced water particulate, but it is also associated with exploration and corrosion maintenance activities (i.e., galvanic anodes). As was not recorded in produced water and its concentration in sediment is not attributable to the discharge. The bioassays with the marine bacterium *Vibrio fischeri* and the sea urchin *Paracentrotus lividus*, have not generally shown sediment toxicity although the produced water toxicity, probably for the swift dilution process of produced water discharge into the sea.

Gorbi et al. (2007, 2008) developed a monitoring protocol with caged mussels to evaluate the potential ecotoxicological effects caused from the off-shore platforms. They transplanted native mussels from an Adriatic reference site to two different areas: a platform area with produced water discharge and another site without discharge. After the translocation period, trace metals were analysed in mussel tissues and early biological responses were detected at several cellular targets. The variations of chemical and biological responses were influenced by fluctuations of biological and environmental factors rather than the effects of platform activities. The effects of seasonality can be more pronounced in certain periods and significantly influence responses of caged organisms. The authors only observed an higher bioavailability for zinc and cadmium close to the platform without discharge, suggesting the influence of galvanic anodes for cathodic protection.

Fattorini et al. (2008) provided an extended 5 year data-set for basal concentrations of several trace metals in Adriatic mussels sampled on off-shore platforms with produced water discharge. While the majority of elements revealed seasonal changes mostly related to phytoplanctonic blooms and reproductive cycle, different fluctuations were observed for arsenic, not correlated with gonadic development, neither with other elements. The marked annual and geographical variations observed for this element suggested the influence of oceanographic or hydrological factors like salinity, of particular relevance for the Adriatic considering the elevated variability of environmental and meteorological conditions in this basin. The authors excluded the anthropogenic impact of exploitation activities, with the only exception of a certain enrichment of cadmium and zinc, probably associated to the use of anodic electrodes.

Tornambè et al. (2012) studied the toxicity of diethylene glycol (chemical additive largely used during oil and gas exploitation by offshore platforms) and its combined effects with produced waters by means acute bioassays with marine/estuarine species. They observed that diethylene glycol is toxic for marine/brackish organisms at concentrations not considered dangerous for the marine environment (orders of g/l)(Group of Experts on the Scientific Aspects of Marine Environmental Protection [GESAMP], 2002) (United Nations [UN], 2011) and normally not detected in Adriatic produced waters (2-13 mg/l) (Cianelli et al., 2008). Besides the results of toxicity tests showed that the presence of diethylene glycol in Adriatic produced waters may alter their toxicity; in fact the addition over 5 g/l has produced synergistic effects. The authors believe that safe threshold concentration of 3.5 g/l (established in Italy) could be considered acceptable for diethylene glycol in co-exposure with produced waters but it should be necessary to study the co-solvency mechanisms between water and glycols because they can act as co-solvents, greatly increasing the solubilization and transport of organic contaminants including BTEX (benzene, toluene, ethylbenzene and xylene), PAHs (polycyclic aromatic hydrocarbons) and alkanes (Sorensen et al. 2004).

Gorbi et al (2009) also studied the toxicity of diethylene glycol alone and in co-exposure with produced waters but using biomarkers. They investigated if diethylene glycol induces direct molecular/cellular effects in marine organisms, or indirectly modulate those of produced water. Sea bass (*Dicentrarchus labrax*) were exposed to diethylene glycol dosed alone or in combination with produced water. Biomarker results did not reveal marked effects of diethylene glycol dosed alone and with produced water, with the only exception of a slight genotoxic damage observed at an exposure dose higher than the maximum allowed limit (3.5 g/l) and of levels normally detected in Adriatic produced water.

Manfra et al. (2010) characterized three produced waters originated from Adriatic gas platforms by chemical analysis and toxicity tests on test-organisms belonging to different trophic levels such as bacteria, algae, crustaceans and fishes. Some differences among the produced waters were observed both for toxicity and chemical composition: the highest toxicity was recorded in the produced waters containing the highest concentrations of some metals (barium, manganese and zinc) and/or volatile aromatic compounds (BTEX). Finally, the authors observed that a filtration treatment of produced waters before their discharge into the sea reduces their toxicity and consequently it may decrease the ecological risk associated to the discharge. As already reported in Mariani et al. (2004), produced water particle presence induces toxicity due to chemical effect of contaminants and/or to particle mechanical effects.

5. Conclusion

The focal intend of this paper has been to explain the importance of use of an integrated chemical and ecotoxicological approach, in wide-ranging for environmental quality assessment and in particular for offshore platform monitoring. In fact, the combination of chemistry and ecotoxicology permits to evaluate the presence of chemical pollutants, their bioavailability, and the adverse effects. Only applying toxicity tests it is possible also see effects of contaminant mixtures and discover effects even if due to contaminants that have not been detected chemically.

Regarding field studies of the Adriatic Sea, quite limited contamination and toxicity were observed in presence of offshore gas installations and/or produced water discharge. Certainly, the principal environmental effects are recorded in sediments and biota, probably due to the nearness of platform anodes, to primary contaminants linked to produced water particles and also to natural regional gradient of some contaminants (e.g. arsenic levels). Although, the potential hazard area is limited (some meters) because the Adriatic platforms drain only small volumes of effluent into the sea and the dilution process is rapid in the near field (Cianelli et al. 2008, 2011). All results obtained for Adriatic platforms confirmed the utility of using ecotoxicology as an additional and complementary contribution to chemical analysis for monitoring offshore activities. Besides in these years Trabucco et al., n.d. provide an main background on each investigation that may be done to assess environmental impacts of offshore platforms, including chemical analysis and bioassay.

6. References

Adams, S.M. & Tremblay, L.A. (2003). Integration of chemical and biological tools in environmental management and regulation. *Australian Journal of Ecotoxicology*, Vol.9, pp.157-164

Ahlf, V. & Heise, S. (2005). Sediment Toxicity Assessment. *Journal Soils & Sediments,* Vol.5, No.1, pp.16-20

Assomineraria (2011). Le previsioni dell'upstream petrolifero per il 2011. Mediapoint & Communications. Gennaio 2011 (sito web www.assomineraria.org)

Beiras, R., Marigomez, I. & Lehtonen, K.K. Biological Tools for Marine and Estuarine Ecosystem Protection. Personal Communication rbeiras@uvigo.es, ionan.marigomez@ehu.es, kari.lehtonen@ymparisto.fi

Chapman, P.M. (2007). The interconnected roles of chemistry and biology (ecotoxicology and ecology) in evaluation of marine environmental quality. *Biologia Marina Mediterranea*, Vol.14, No.1, pp.10-16

Cianelli, D., Manfra, L., Zambianchi, E., Maggi, C., Cappiello, A., Famiglini, G., Mannozzi, M. & Cicero, A.M. (2008). Near–field dispersion of Produced Formation Water (PFW) in the Adriatic Sea: an integrated numerical and chemical approach. *Marine Environmental Research,* Vol.65, pp.325-337

Cianelli, D., Manfra, L., Zambianchi, E., Maggi, C. & Cicero, A.M. (2011). Modelling and Observation of Produced Formation Water (PFW) at Sea. In: *Fluid Waste Disposal,* Canton, K.W. (Ed.), 113-135, Nova Science Publishers, Inc., ISBN 978-1-60741-915-0, New York

De Biasi, A.M., Fabi, G., Pacciardi, L., Spinelli, O., Micheli, R., Puletti, M. & De Ranieri, S. (2006). Metalli pesanti e idrocarburi policiclici aromatici in prossimità di una piattaforma di estrazione: 3 anni di osservazioni (Adriatico settentrionale). *Biologia Marina Mediterranea*, Vol.13, No.2, pp.332-333

E&P Forum/UNEP (1997). Environmental management in oil and gas exploration and production. UNEP IE/PAC Technical Report 37. E&P Forum Report 2.72/254. ISBN 92-807-1639-5, pp.1-76

Enerdata (2011). Global Energy Statistical Yearbook 2011. http://yearbook.enerdata.net

Fattorini, D., Notti, A., Di Mento, R., Cicero, A.M., Gabellini, M., Russo, A. & Regoli, F. (2008). Seasonal, spatial and inter-annual variations of trace metals in mussels from the Adriatic sea: a regional gradient for arsenic and implications for monitoring the impact of off-shore activities. *Chemosphere*, Vol.72, pp.1524-1533

GESAMP (2002). (IMO/FAO/UNESCO-IOC/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Revised GESAMP Hazard Evaluation Procedure for Chemical Substances Carried by Ships. Rep. Stud. GESAMP No. 64, 126 pp.

Gorbi, S., Benedetti, M., Bocchetti, R., Virno Lamberti C., Moltedo, G., Di Mento, R., Fattorini, D., Pisanelli B., & Regoli, F. (2007). Use of caged mussel *Mytilus galloprovincialis* in an ecotoxicological approach to assess environmental impact in offshore activities. *Rapp. Comm. int. Mer Medit.*, Vol.38

Gorbi, S., Virno Lamberti, C., Notti, A., Benedetti, M., Fattorini, D., Moltedo, G. & Regoli, F., (2008). An ecotoxicological protocol with caged mussels, Mytilus galloprovincialis, for monitoring the impact of an offshore platform in the Adriatic sea. *Marine Environmental Research,* Vol.65, pp.34-49

Gorbi, S., Benedetti, M., Virno Lamberti, C., Pisanelli, B., Moltedo G. & Regoli, F. (2009). Biological effects of diethylene glycol (DEG) and produced waters (PWs) released from offshore activities: a multi-biomarker approach with the sea bass *Dicentrarchus labrax*. *Environmental Pollution,* Vol.157, pp.3166-3173.

Henderson, B., Grigson, S.J.W., Johnson, P. & Roddie, B.D. (1999). Potential impact of production chemical on the toxicity of produced water discharges from North Sea oil platforms. *Marine Pollution Bulletin,* Vol.38, No.12, pp.1141-1151

Maggi, C., Berducci, M.T., Bianchi, J., Giani, M. & Campanella, L. (2009). Methylmercury determination in sediment and marine organisms by Direct Mercury Analyser. *Analitica Chimica Acta*, Vol.641, pp.32-36

Manfra, L., Moltedo, G., Virno Lamberti, C., Maggi, C., Finoia, M.G., Gabellini, M., Giuliani, S., Onorati, F., Di Mento, R. & Cicero, A.M., (2007). Metal content and toxicity of produced formation water (PFW): study of the possible effects of the discharge on marine environment. *Archives of Environmental Contamination and Toxicology,* Vol.53, pp.183-190

Manfra, L., Maggi, C., Bianchi, J., Mannozzi, M., Faraponova, O., Onorati, F., Mariani, L., Tornambè, A., Virno Lamberti, C. & Magaletti, E. (2010). Toxicity evaluation of produced formation waters after filtration treatment. *Natural Science,* Vol.2, No.1, pp.33-40.

Manoukian, S.. Spagnolo, A., Scarcella, G., Punzo, E., Angelini, R. & Fabi, G. (2010). Effects of two offshore gas platforms on soft-bottom benthic communities (northwestern Adriatic Sea, Italy). *Marine Environmental Research,* Vol.70, pp. 402-410

Mansour, M. (1993). Fate and Prediction of Environmental Chemicals in Soils, Plants and Aquatic Systems. Lewis Publishers, Chelsea, MI

Mariani, L., Manfra, L., Maggi, C., Savorelli, F., Di Mento, R. & Cicero, A.M. (2004). Produced formation waters: a preliminary study on chemical characterisation and acute toxicity by using fish larvae (*Dicentrarchus labrax* L.,1758). *Fresenius Environmental Bulletin,* Vol.13, No.12a, pp.1427-1432.

OSPAR, 2009. Assessment of impacts of offshore oil and gas activities in the North-East Atlantic. Ospar Commission, London, No.453/2009, ISBN 978-1-906840-93-8, 40 pp.

Piva, F., Ciaprini, F., Onorati, F., Benedetti, M., Fattorini, D., Ausili, A. & Regoli, F. (2009). Assessing sediment hazard through a weight of evidence approach with bioindicator organisms: a practical model to elaborate data from sediment chemistry, bioavailability, biomarkers and ecotoxicological bioassays. *Chemosphere*, Vol.83, pp.475-485

Rabalais, N.N., McKee, B.A., Reed, D.J. & Means, J.C. (1992). Fate and effects of produced water discharges in coastal Louisiana, Gulf of Mexico, USA. In: *Produce Water.*, J.P. Ray, F.R. Engelhart, (Eds.), 355-369, Plenum Press, New York

Scott, K.A., Yeats, P., Wohlgeschaffen, G., Dalziel, J., Niven, S. & Lee K. (2007). Precipitation of heavy metals in produced water: Influence on contaminant transport and toxicity. *Marine Environmental Research,* Vol.63, pp.146-167

Setan, H. & Othman, R. (2006). Monitoring of Offshore Platform Subsidence Using Permanent GPS Stations. *Journal of Global Positioning Systems*, Vol.5, No.1-2, pp.17-21

Sittig, M. (1991). Handbook of toxic and hazardous chemicals and carcinogens. Ed. Park Ridge, N.J., Noyes Data Corporation, 3rd ed

Sorensen, J.A., Gallagher, J.R. & Hawthorne, S.B. (2004). Gas industry groundwater research program; final report for U.S. Department of Energy, National Energy Technology Laboratory. Cooperative Agreement No. DE-FC26-98FT40321; EERC Publication 2004-EERC-07-01; Energy & Environmental Research Center: Grand Forks, ND

Stromgren, T., Sorstrom, S.E., Schou, L., Kaarstad, I., Aunaas, T. & Brakstad, O.G. (1995). Acute toxic effects of produced water in relation to chemical composition and dispersion. *Marine Environmental Research,* Vol.40, pp. 147–169

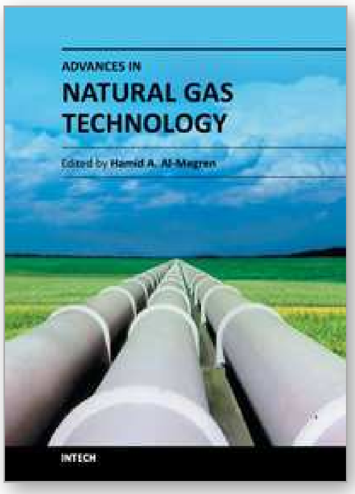
Tornambè A., Manfra L., Mariani L., Faraponova O., Onorati F., Savorelli F., Cicero A.M., Virno Lamberti C., Magaletti E. (2012). Toxicity evaluation of diethylene glycol and its combined effects with produced waters of off-shore gas platforms in the Adriatic Sea (Italy): Bioassays with marine/estuarine species. *Marine Environmental Research* doi:10.1016/j.marenvres.2011.12.006

Trabucco, B., Cicero, A.M., Gabellini, M., Virno Lamberti, C., Di Mento, R., Bacci, T., Moltedo, G., Tommassetti, P., Panfili, M., Marusso, V. & Cornello, M. (2006). Study of the soft botom macrozoobenthic community around an offshore platform (Central Adriatic Sea). *Biologia Marina Mediterranea*, Vol.13, Vol.1, pp.659-662

Trabucco, B., Maggi, C., Manfra, L., Mannozzi, M., Nonnis, O., Cicero, A.M., Di Mento, R., Gabellini M. & Virno Lamberti, C. n.d. Monitoring of impacts of offshore platforms in the Adriatic Sea (Italy). *Natural Gas*, InTech ISBN 979-953-307-567-8

UN (2011). Globally Harmonized System of Classification and Labelling of Chemicals (GHS), fourth revised ed. United Nations, New York and Geneva

Volpi Ghirardini, A. & Pellegrini, D. (2001). Toxicity bioassays in water and sediment quality assessment of marine and transitional environments: suggestions for the choise, set up, evaluation and application methods. *Biologia Marina Mediterranea*, Vol.8, No.2, pp.1-16



Advances in Natural Gas Technology

Edited by Dr. Hamid Al-Megren

ISBN 978-953-51-0507-7
Hard cover, 542 pages
Publisher InTech
Published online 11, April, 2012
Published in print edition April, 2012

Natural gas is a vital component of the world's supply of energy and an important source of many bulk chemicals and speciality chemicals. It is one of the cleanest, safest, and most useful of all energy sources, and helps to meet the world's rising demand for cleaner energy into the future. However, exploring, producing and bringing gas to the user or converting gas into desired chemicals is a systematical engineering project, and every step requires thorough understanding of gas and the surrounding environment. Any advances in the process link could make a step change in gas industry. There have been increasing efforts in gas industry in recent years. With state-of-the-art contributions by leading experts in the field, this book addressed the technology advances in natural gas industry.