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IUPAC Technical Report

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Maritime pollutants in shipping and commercial European ports based on relevant physical and biogeochemical environmental parameters (IUPAC Technical Report)

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Abstract: Ports are closed or semi-closed coastal systems with limited water circulation, poor flushing and weak tidal exchange. They are characterized as pollution hotspots or areas of stagnation with a variety of maritime pollutants. Nowadays, shipping and port managers aim to address environmental risk in their operations, striving to achieve suitable environmental management systems and environmental policies. In that way, environmental impacts are thoroughly considered, actions to minimize and prevent these effects are identified while human activities for prevention, reduction and mitigation of harmful consequences are managed. The current project provides details of quality and performance indicators, based on physical and biogeochemical environmental parameters required to monitor and audit the effectiveness of environmental management system and environmental policy applied in ports. These indicators will be used as powerful tools strengthening sound decisions when developing, shaping and evaluating national and local environmental management systems and policies. The selected indicators are described and their monitoring processes are presented and discussed. Examples of selected best environmental practice from various port authorities are included.

Keywords: environmental management system; environmental policy; IUPAC Chemistry and the Environment Division; maritime pollutant; monitoring; port; quality and performance indicator.

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1 Introduction

Ports and harbors where there are high levels of vessel, urban and industrial activity may be considered as contaminated areas. They are marine basins, which through physical topography, bathymetry and/or the various technical constructions, are characterized as closed or semi-closed coastal systems with limited water circulation. This can lead to pollution hotspots [1] or areas of stagnation due to poor flushing and tidal exchange. In general, chemical pollution is exceptionally high in ports and harbors influencing wider areas. The pollutants associated with antifouling paints, the use of hydrocarbons, the release of untreated contaminated water and unregulated industrial activity all contribute to the contaminants found in water and settle in the underlying sediment of the sea bed. The result is environmental degradation with potential negative impacts on the well-being of marine biocommunities and consequences upon the local and regional economy. The situation is critical as in the last decade ports around the world have extremely grown due to keeping abreast of drives for international trade and the need to create hub-port distribution centres (e.g. Southampton, UK) [2].

A wide range of pollutants found in the air, the sea water column, marine sediments and marine biota of ports, are more or less related to the maritime industry. The ubiquitous problem of TBT and its log-term legacy is a notable example [3, 4]. Pollutants derive from maritime traffic (cargo spills, oily bilge discharges, ballast water [often containing exotic species], antifouling paints and sewage), port activities (sewage, cooling waters, spills), solid waste (dumping), construction and maintenance, dredging (releasing contaminants) [5], shipyards and repair zones [6].

Nowadays, both shipping and port managers aim to address environmental risk [7]. Therefore in line with other major industries, they strive to achieve suitable EMS and EP. Accordingly, successful port environmental management should consider operations with an emphasis on those with potential to significantly impact the surrounding environment, and then identify actions to prevent or minimize these aspects [8]. An EMS furnishes the processes and procedures to control and improve the environmental consequences. An EP should correspond to any deliberately taken action to manage human activities aiming at prevention, reduction and mitigation of harmful effects, incorporating issues such as air and water pollution, waste and ecosystem management, biodiversity and natural resources protection.

The effectiveness of environmental management actions put in place requires monitoring and assessment and for this purpose physical, biogeochemical and ecological environmental parameters may be utilized as performance indicators. The environmental parameters should incorporate water, sediment and air quality in addition to species and community characteristics [9, 10]. Also, the physicochemical characteristics of the receiving waters into which chemical contaminants will be deposited require consideration as they have potential to influence chemical speciation, mobility as well as pollutant toxicity and bioavailability. For example, it has long been known that fine sediment, often associated with sluggish port waters, can bind strongly to chemical species, leading to a "reservoir" [3] of slowly released pollutants, giving long term effects which may "cascade" upwards to the human food chain [11].

Port managers and environmental regulators should aim at: rational planning of pollution control activities; identification of hot spots and their prioritization; assessment of trends, and evaluation of pollution control effectiveness. This would enable recommendation of remedial measures to improve environmental quality and the continual improvement of environmental performance. Thus, these indicators would provide valuable information as they are environmental performance indicators of the quality of the respective environmental (EMS, EP) actions. Consequently, they should support sound decisions when developing, shaping and evaluating national and local EMS and EP.

An important issue of the port environmental management is the enforcement of training and educational package. Its main aims are to encourage the culture of monitoring and reporting as well as to promote campaigns focusing on being environmentally aware.

2 Quality and performance indicators

The most significant and effective indicators for the characterization of quality and performance should be selected and quantified. Indicators are classified in four groups according to the respective matrix, including sea water, sea sediment, marine biota and air. All indicators are thoroughly described and their monitoring procedures fully discussed.

2.1 Sea water indicators

There is a wide range of water indicators that can be used. However, some effort should be put to select only the most effective ones, which means indicators that are strongly relevant with the measuring purpose, ask for a simple monitoring procedure and an easy interpretation while they furnish with reliable information. Table 1 lists the set of final sea water quality and performance indicators selected for this project. The numbering does not imply any order of importance.

Floating debris refers to a wide variety of foreign matter floating or remaining suspended in the water column [12] such as aluminium cans, bottles, plastics, street litre, paper, etc. Their origin can vary and they are introduced into the coastal marine environment through the sea, the land or the atmosphere covering long distances from the source to the deposition [13]. Floating debris is usually quite persistent in bio degradation and causes significant environmental impacts. It is responsible for an aesthetic pollution, causes economic losses and has the potential to put at risk humans and marine animals. The best way for the floating debris collection is by using specialized vessels. After being removed, wastes are deposited in storage containers according to the material and then transferred to specific plans for treatment, mainly reuse. Information about the type, amount and possible source of the floating debris in relation to the period of time and the prevailing conditions such as rainfall, wind, sea currents, tides, leaks, etc. are gathered.

The dissolved oxygen concentration (DO) refers to the amount, mass or volume of oxygen dissolved in a certain volume or mass of water. It represents the level of free oxygen present in water and is vital to many forms of life. It enters to the sea from the atmosphere or it is produced as a photosynthesis product. There is also the down welling mechanism (sinking of surface water) flushing the oxygen rich surface water through the deep sea by the conveyer belt of the global ocean, however, this mechanism cannot be applied to the semi closed coastal marine basins. Among the various methods for the DO determination, we will refer to the sensor method that uses a DO meter and a sensor (probe), doing the testing in the field.

BOD measures the concentration of oxygen consumed by aerobic micro-organisms in decomposing the biodegradable organic matter present in a water sample. As BOD affects the DO amount, high BOD levels have the same consequences as low DO which are environmental pressure on marine organisms leading to suffocation and death. BOD determination requires two measurements at each site, one immediately and another after incubation in the dark at 20 °C for 5 days. The difference in DO levels between the first and second measurement gives the BOD [14].

Table 1: List of sea water quality and performance indicators.

	Indicator
1	Floating debris
2	Dissolved oxygen (DO)
3	Biochemical oxygen demand (BOD)
4	Fecal bacteria
5	Sea water turbidity
6	pH
7	Sea water temperature

Fecal bacteria, such as coliforms and fecal streptococci, indicate possible sewage contamination as both groups are frequently found in human and animal faeces. In general, they are not considered as significantly harmful however, their presence may indicate pathogenic bacteria and viruses. Possible sources are waste water treatment plants, storm run-off, livestock, etc. while the caused impacts include possible health risk, cloudy waters and unpleasant odours as well as increased oxygen demand for degradation purposes. It is considered that enterococci are the best bacterial indicators for marine waters. Laboratory analysis is described in references [14, 15] however, due to the complexity of the procedure, field analysis is not recommended. The method suggested is the multi-tube fermentation one which is also applied by the port of Dover. According to it, specific amount of sample is added to tubes with a nutrient broth and the mixture is left for incubation at a standard temperature for a standard period of time. The presence of bacteria produces turbidity in the culture medium, causes pH change, and/or develops gas. In a following step the most probable number of bacteria is obtained. Values are expressed as MPN per 100 mL of sample. The port of Dover carries out this process twice a year, in August and February [16].

The turbidity of the water column refers to the amount of suspended materials present, including silt, clay, sand, phytoplankton species and detrital matter. Increased water turbidity corresponds to decreased water clarity. It should be kept in mind that high primary productivity results in higher turbidity values while increased turbidity (from a variety of reasons) eliminates the amount of sunlight needed from submerged marine flora, therefore there is a fine balance that should be kept. Turbidity is a water parameter recorded in the field either with a secchi disk or a turbidimeter. The former procedure relies on the secchi disk depth which is the maximum depth in metres at which the distinction between the black and white quadrants of the disk can be done. The later gives turbidity in absolute values reported in mephelometric turbidity units.

According to the Green Book of IUPAC [17], pH is defined in terms of the activity of hydrogen ions in solution. Marine water has a high buffering capacity for pH and therefore changes in pH values tend to be small and localised. In the marine environment, changes in pH values may affect marine biota and ecosystems as well as the solubility and toxicity of chemicals and heavy metals. In general, pH is considered as a fundamentally significant parameter for various chemical as well as biological processes that take place in the marine ecosystem. The pH of water depends on natural influences (such as the presence of carbonate minerals) and anthropogenic ones (like emissions from mining and smelting operations as well as combustion of fossil fuels and chemicals from agricultural and industrial runoff and wastewater discharges). As the global ocean absorbs a high fraction of the anthropogenic carbon dioxide emissions into the atmosphere, there is an ocean acidification reported lately. In a port area, the pH of seawater may change due to man-made causes. It is measured in the field by using a glass electrode.

Sea water temperature is a physical parameter that exerts a strong influence on the biogeochemistry of the marine environment, mainly affecting water density, chemical solubility and metabolic rate. It can be measured by a thermometer or by using a CTD oceanographic instrument that determines conductivity, temperature and depth.

2.2 Sea sediment indicators

Table 2 lists quality and performance indicators for sea sediment selected for this project.

Grain size refers to the diameter of individual grains of sediments. Grain size (particle size) distribution is a physical property of sediments and soils that is commonly used for classification purposes. It is considered as an easy, inexpensive and relatively fast method that gives crucial information about the trends in surface processes related to dynamic conditions of transportation and deposition as well as kinetic reactions and the affinities of fine grained particles and contaminants. Grain size analysis can be done in many ways, like using sieves, X-rays or even laser beams. Methods commonly used are the particle size analysis using a Coulter LS particle Size Analyzer [18], the multi wavelength particle size analyzer [19], the ASTM D422 Standard Test Method for Particle-Size Analysis of Soils [20], a specific sieving program producing seven size fractions [21],

Table 2: Selection of quality and performance indicators for sea sediment.

	Indicator
1	Grain size
2	Redox potential
3	Concentration of heavy metals (Hg, Pb, Cu, Ni, Co, Zn, Cd, Sn, Cr, Fe) and As
4	Concentration of polycyclic aromatic hydrocarbons (PAHs)
5	Concentration of polychlorinated biphenyls (PCBs) and tributyltin (TBT)
6	Concentration of mineral oils
7	Benthic foraminifera

the Micromeritics Sedigraph 5120 instrument [22] and the sieving technique according to Folk and Ward [23]. Colour can be estimated from comparisons with the standard Munsell soil colour chart [24].

Redox potential, according to the Green Book of IUPAC, is the reduction/oxidation potential of a compound measured under standards conditions against a standard reference half-cell. It is a useful "tracer" for oxygen bearing and consuming processes in the water-sediment column. Redox conditions in surface sediments depend on the degree of organic enrichment and can be assessed by measuring the vertical redox potential profile (expressed in mV) in the top 15 cm [25]. Redox potential shows a decrease with depth due to the decrease in the DO concentration while negative values represent an anoxic environment and the presence of hydrogen sulfide. It can be measured by pressing a redox electrode into an intact sediment core immediately after its collection to avoid changes to its values due to biogeochemical processes. Redox potential profiles can be measured applying a specific methodology [26] that allows the transfer of the core while maintaining the *in situ* structure and stratification.

Heavy metals and arsenic include metals and metalloids with a density greater than 4 $g \cdot cm^{-3}$. They enter the environment through natural and anthropogenic processes causing severe environmental problems as they are accumulated in reservoirs by biological and geochemical mechanisms. It has been shown by many authors that large amounts of heavy metals are bound in the fine grain fraction (< 63 μm) of the sediment [27, 28]. Commonly, the dried homogenized sediment samples are sieved through a 63 μm screen and kept in clean plastic containers ready for analysis. The powder samples, less than 63 μm, are used for heavy metal analysis. Total metal concentration can be measured by acid digestion in an airtight Teflon system [29]; digestion by *aqua regia* and concentrated HF using microwave heating and metal concentration measurement by AAS equipped with a THGA graphite furnace, Mercury Hydride System and a flame system [30]; microwave acid digestion (HNO_3 and *aqua regia*) and determination by flame or furnace AAS [31]; digestion with HNO_3, HF, *aqua regia* and $HClO_4$ and determination by AAS [32]; a three-step treatment of sample drying, acid digestion (by HF-$HClO_4$-HNO_3 mixture in Teflon beakers) and AAS analysis [33]; acid digestion (HNO_3, $HClO_4$ and HF in Teflon cups) followed by heating, cooling and determination by AAS [34]; digestion with a mixture of hydrofluoric and perchloric acids in a platinum crucible, evaporation, dissolution and determination by flame AAS [35].

Metal bioavailability is a critical parameter for the metal risk assessment as total metal concentrations cannot predict environmental impacts. It can be described by the metal availability in the sediment, followed by the metal uptake by the marine biota and finally the metal availability, accumulation and effect in the species. It is well supported that the bioavailable fraction is not considered as a fixed value for given sediment but it may vary according to the biological receptor and the sediment depth [36]. For the determination of the environmentally mobile metal fraction (apart from refractory sample matrix compounds, such as quartz, silicates, titanium dioxide, alumina, etc., that are excluded from most aqueous transport mechanisms of pollution), the procedure refers to extraction and/or dissolution in acid using microwave heating and analysis by GFAA, ICP-AES or ICP-MS [37] and a weak acid digestion and determination by AAS with air–acetylene flame [38]. According to Siqueira and Aprile (2011), the bio-available fraction of the metals is the main environmental risk for aquatic ecosystems. Metals determined are considered potentiality bio-available, and an increase of the oxygen levels in the water column allows a remobilization of the metallic elements to the trophic net [39]. The fraction (expressed in%) of bio-available metals in the sediments can be described by the expression [40]: BA = MC/TC**,** where: MC is the concentration of metals in the mobile phase and TC the total concentration of the metal in the samples.

PAHs are lipophilic anthropogenic chemicals exhibiting mutagenic, carcinogenic, and teratogenic potential. They are characterized by a persistent nature and they tend to accumulate in marine sediments. Sedimentary PAHs cause severe impacts to both benthic (directly) and pelagic (indirectly) marine species. They are considered as a toxic group of environmental contaminants and they are included in the European Union and US Environmental Protection Agency priority pollutant lists. The determination and quantification of PAHs in sediment samples can be performed using extraction with acetone/n-hexane [41] and applying GC-MS [42]; extraction by a Soxhlet apparatus [43] and analysis GC-MS [44] with a capillary column; an extraction and fractionation technique based on the SW-846 test methods while quantification and qualification of PAHs are performed by the modified method of USEPA 8270 [45] by a capillary gas chromatograph [19]; an extraction procedure by using pressurized solvent [46] while PAHs fractionation and analysis is performed by activated silica gel column and a GC-MS [47, 48]; extraction and purification by gel permeation chromatography and analysis by HR GC-MS [49]; following the EPA Method 8310 and using for analysis HPLC with ultraviolet and fluorescence detectors**.**

PCBs are environmental contaminants regulated by the Stockholm Convention of POPs) [50], and are included on the OSPAR List of Chemicals for Priority Action due to their persistence, potential to bioaccumulation, and toxicity. The determination of PCBs in sediment generally involves extraction with organic solvents [51, 52], clean-up and gas chromatographic separation with electron capture detection or mass spectrometry [53]. There is also the EPA-Method 8080 [54] providing gas chromatographic conditions for the detection of certain organochlorine pesticides and PCBs at mass fraction of $\mu g \cdot kg^{-1}$. Commercial polychlorinated biphenyl mixtures (known as Aroclors) and chlorinated pesticides can be identified and quantified by extracting the sediment with a water/methanol/hexane mix and analysing an aliquot of the hexane layer on a GC-ECD, [55]. A detailed procedure for the extraction and clean up of sediment samples for PCBs analysis using the Soxhlet extraction technique by SW-846 Method 3540C for subsequent analysis by SW-846 Method 8082 is described by QEA, [56].

TBT is one of the most hazardous contaminant in the marine environment. Its main source of introduction is TBT antifouling paints used on ship hulls. It affects not only marine organisms that are attached to the hull (like barnacles, algae, tube worms, etc.) but also non-target ones (like oysters and mussels) causing abnormal shell development and imposex [57]. It affects negatively various invertebrates (leading to sterility or even death) [58] and it is accumulated in fish, dolphins, seals whales and other sea mammals. TBT in sediment samples can be determined by GC-MS after treatment with a solution of acetic acid/methanol with ultrasonic shredder [59]; GC-MS after spiking with isotopically labelled analyte, pressurized liquid extraction and Grignard derivatization [60]; GC-ICP-MS after treatment with a species-specific isotope dilution method [61]; a rapid and precise method performed by species specific IDMS analysis using a CGC-ICP-MS [62]; a liquid chromatographic method with fluorimetric detection using fisetin as fluorogenic reagent [63].

Mineral oils are among the most significant organic pollutants in the environment. The fraction of TPH between C10 and C40 is considered as mineral oil. TPH is a term used to describe a mixture of several hundreds of chemical compounds deriving from crude oil. As TPH are released to the water mass trough spills or leaks, the lighter fractions float in the water column forming thin surface films while the heavier ones tend to accumulate in bottom sediments affecting bottom feeding organisms. TPH can be quantified by GC-FID. Consequently, mineral oils can be quantified by calibrating the GC with an appropriate hydrocarbon mixture that mirrors the condition encountered in practice [64]. Frank and Klee [65] followed an extraction by an apolar solvent with a boiling point between 36 °C and 69 °C (like, hexane), purification of the extract by passing over Florisil, concentration by N_2 blow down and analysis by GC-FID (ISO 9377-2) [66]. The fraction eluting on an apolar (HP-1, HP-5) column between decane (C_{10}) and tetracosane (C_{40}) is summed for quantitation.

Foraminifera are a class of amoeboid protists, networks of "granuloreticulate pseudopodia." Most of species live on or within the seafloor sediment characterized therefore as benthic ones, while there is still a limited number of species that float in the seawater column at various depths, characterized as planktonic ones. They have complex life cycles with sexual and asexual generations. Most of them have a mineral shell but there are some naked forms as well. Foraminifera are among the most abundant unicellular organisms in the modern ocean. They are studied from a geological and biological perspective, being useful tools in paleo-ecological and paleoclimatic reconstructions. Benthic foraminifera are an important constituent of the sea biomass. In oligotrophic but well oxygenated environments, foraminiferal communities are restricted to the surficial sediments and consist of epifaunal, or surface dwelling taxa. In eutrophic environments with limited pore water oxygen amount, foraminiferal communities are dominated by infaunal taxa [67]. Nowadays, benthic foraminifera are more and more used as environmental indicators of natural and/or anthropogenic stress in coastal and marginal marine environments, considered as precision tools for bio-monitoring [68, 69].Calcifying foraminifera are expected to be endangered by ocean acidification [70]. For the analysis of benthic foraminifera, Rose Bengal stained (living) [68] and dead replicates should be taken [71, 72].

2.3 Marine biota indicators

Table 3 lists quality and performance indicators for marine biota.

Marine algae are among the most ancient members of the plant kingdom forming a group of some of the simplest organisms that contain the chlorophyll pigment. They have an important role in the ecosystem of marine life and they are found in abundance in coastal marine areas where they usually grow attached to a hard surface in relation to the sunlight availability and the amount of nutrients present. Nevertheless, their excess growth causes eutrophication leading to dissolved oxygen depletion. In order to ensure a healthy coastal marine environment, algae content should be in balance [17]. Algae monitoring has to be done on a seasonal basis in carefully selected sites. The port of Dover [73] follows a very easy procedure according to which each site is marked by two signs at a specific distance the one of the other, sites are visited by a survey vessel and photographs are taken. Back to the office, the percentage cover of algae at each side (in terms of area fraction) is calculated.

Trawling is a method of fishing by pulling a net through the water behind one or more boats permitting the sampling of various species living either within the water column or in the seabed. This method helps drawing conclusions about the environmental status as the occurrence of a high variety of species corresponds to a healthy environment. The monitoring of marine species is based on sampling four times a year in order to determine the seasonal variation. Usually, species are caught, kept alive in water containers, identified, measured, weighted and returned to the harbor.

Ornithological data is important in ensuring that port development and maintenance projects are undertaken appropriately with regard to protected species, in a way that minimal impacts are created to these species during their breeding season. Ornithological surveying is the bird activity monitoring. In Dover ports [74] it refers to counting and mapping all birds including any breeding activity within the limits of the port and those which are within 50 m radius of the port limits. Also, flight paths are noted for birds in transit from one area of the port to another. Winter Bird Surveys are conducted twice between October and February. Breeding Bird Surveys are also conducted bi-monthly but over the breeding season between March and May inclusive. The outcome helps in understanding and predicting the consequences of climatic change, port operations

Table 3: Selection of quality and performance indicators for marine biota.

	Indicator
1	Algae
2	Trawling
3	Ornithological surveys
4	Benthic fauna
5	Concentration of chemicals (heavy metals, organochlorine compounds, dioxin and furan) in fish
6	*Argopecten gibbus* (a calico scallop)

and changes in land uses on birds. Surveys over long periods of time are particularly useful in order to find out alterations about abundance, distribution, and overall productivity of breeding bird populations.

Benthic fauna refers to marine animals found on (epifauna) and in (infauna) the seabed. A benthic fauna survey is important from an ecological point of view as it furnishes with information whether an oxygen deficiency has occurred at a specific site. Monitoring is based on sampling four times a year to catch seasonal variation. The sampler can be either grabber or a corer. Samples are sieved and marine species immediately preserved. Tidal data are recorded. Then, species and sediment type are identified. In this way suggestions about environmental disturbance are allowed, as benthic communities are highly affected by the environmental parameters controlling both distribution and diversity variation of benthic fauna.

Chemicals, like heavy metals, organochlorine compounds, dioxin and furan are determined in fish issues to show bioaccumulation of pollutants. Results are used to assess the environmental well being of the area.

Argopecten gibbus is a species of medium-sized edible saltwater scallop, a marine bivalve mollusk in the family Pectinidae. Typical benthos types for *A. gibbus* include unconsolidated sediments made up of hard sand, sand with shell hash, quartz sand and sand gravel. It is characterized by a strong ability for bio accumulation and bio-concentration of toxicants, a motionless endobenthic life style and a rather widespread distribution. Consequently, bivalve mollusks serve as bio-indicators and they have been widely used as sentinel species to monitor environmental contamination [75] as well as in biomarker studies to examine the effects of municipal effluents [76, 77], pesticides [78] and heavy metals [79–81].

2.4 Air indicators

Table 4 lists quality and performance indicators for air.

There are various emission-producing sources related to port operations that emit greenhouse gases and other air pollutants of concern. These sources include port administration vehicles, power plants providing power for administration offices, tenant buildings, electrified cargo handling equipment, fuel-powered cargo handling equipment, ships, harbor craft, trucks, rail locomotives, etc. The relationship of these sources with the port itself is direct or indirect one. The engines at ports create vast amounts of air pollutants that affect the health of workers and people living in nearby communities, contributing dramatically to regional air pollution. Various studies show that diesel exhaust increases cancer risks and it is linked with asthma [82]. Major air pollutants from diesel engines at ports that can affect human health include PM, VOCs, NOx and SOx. HFCs may be emitted in small amounts from leaks in refrigeration equipment such as air conditioning units.

The most common greenhouse gases associated with port-related operations are the combustion related pollutants carbon dioxide, methane and nitrous oxide. Carbon dioxide typically constitutes over 99% of combustion related greenhouse gas emissions. Emissions should be given in terms of carbon dioxide equivalents. The IPCC has established international standard for determining greenhouse emissions for cities [83].

Table 4: Selection of quality and performance indicators for air.

	Indicator
1	Greenhouse gases
2	Ozone-depleting substances [chloro fluoro carbons (CFCs), hydro chloro fluoro carbons (HCFCs), halons, and methyl bromide]
3	NOx, SOx
4	Persistent organic pollutants (POPs)
5	Volatile organic compounds (VOCs)
6	Hazardous air pollutants (HAP)
7	Particulate matter (PM)
8	Dust

Hazardous air pollutants, or toxic air pollutants or air toxics, are those pollutants that cause or may cause cancer or other serious health effects, like reproductive effects or birth defects, or adverse environmental and ecological effects. Most of them derive from human-made sources, such as mobile sources, stationary sources and indoor sources. The United States Environmental Protection Agency is required to control 187 hazardous air pollutants.

The estimation of emissions produced can be based on three data sets, which are source data, activity data and emission factors. The first set refers to data about emissions source characteristics, like size or rating of the engine or power plant, type of fuel burnt, engine technology information, age of the engine, manufacturer, model, etc. The second set details how the source operates over time and how engine loads and/or fuel consumption change by mode of operation, miles travelled by speed, power production rates, etc. The third set provides the means to convert the estimates of energy output or fuel consumption into the pollutant emission rates that are to be modeled.

The approach to be followed can be activity based, surrogate based or hybrid one. The activity based one provides the highest levels of accuracy, utilizing equipment specific source data (like actual engine ratings, actual power consumption, actual fuel consumption, etc.), equipment specific activity data (like hours operated, load factor data, fuel consumption data, vessel call data, etc.) and either source specific emissions test data or emission factors for source categories/equipment types. Emissions are estimated using the following equation:

$$Emissions = Energy\ or\ Fuel\ Consumption \times Emission\ Factor$$

where, *Energy or Fuel Consumption* is the combination of source and activity data while *Emission Factor* represents the emission producing characteristics varying by source types per unit or energy consumption.

The surrogate based approach utilizes “related” data or surrogates to substitute for source data, activity data, energy consumption, and/or emissions per activity. It is typically less accurate than the activity-based approach, which can be significant depending on the surrogate (s) used. Accuracy depends on how close the surrogate matches actual operations. Emissions are estimated using the following equation:

$$Emissions = Activity \times Surrogate\ Emissions / Activity$$
$$Emissions = Surrogate\ Energy\ Consumption \times Emissions\ Factor$$

where, *Activity* refers to port-related operations being modelled (such as ship calls, cargo handling, equipment numbers, fuel purchased, employees, registered vessels, cargo throughput, etc.). *Surrogate Emissions/Activity* refer to emissions from a published study or inventory, etc. per activity (like, ship calls, cargo handling equipment numbers, fuel purchased, employees, registered vessels, cargo throughput, etc.). *Surrogate Energy Consumption* refers to energy consumption surrogates based on published studies, documents, inventories by equipment type, building square footage, vessel type, etc.

The hybrid approach utilizes varying combinations of both activity-based and surrogate based inventories, depending on data availability, surrogates, time constraints, etc. Its accuracy depends on which sources are estimated using surrogates and how close those surrogates match actual operations.

PM is a mixture of solid particles and liquid droplets suspended in the air. Particles are characterized as coarse PM_{10} with an aerodynamic diameter between 2.5 μm and 10 μm, or fine $PM_{2.5}$ with a diameter of 2.5 μm or less. They derive from various sources. Some are emitted directly from their primary sources while others are formed in the atmosphere. According to the California Environmental Protection Agency [84], PM_{10} mass is collected using a high volume sampler and a quartz fiber filter. The PM_{10} standards are expressed as a weight of PM_{10} particles per volume of air (micrograms per cubic meter). Knowledge of the composition of PM_{10} helps indicating the sources of the particles. Routinely measured inorganic ion analyses comprise chloride, nitrate, sulfate, ammonium, and potassium by ion chromatography. Fine matter is a mixture of combustion products emitted into the atmospheric air (primarily formation) and particles which are secondarily formed in the air from gaseous pollutants. $PM_{2.5}$ corresponds to greater health risk than $PM_{10.}$ According to the California Environmental Protection Agency [84], $PM_{2.5}$ mass is collected using a low volume sampler and a small Teflon filter. As the $PM_{2.5}$ sampler collects much less mass, the samples are weighed to the nearest microgram by special, ultra-sensitive balances. X-ray fluorescence analysis determines the concentration of 28 elemental constituents in the $PM_{2.5}$. Ion chromatography is applied for the ion analysis of the water soluble ionic constituents after treatment with nitric acid. Thermal optical pyrolysis can also be applied for the determination of the organic fraction of the carbon and the elemental carbon.

3 International port authority website research

Table 5 gives the outcome of an international port authority website research with the main environmental actions for each port.

4 Conclusions

Maritime activities exert pressures on the environment affecting its state. Monitoring the environmental state helps informing managers as to whether management objectives have been met. An EMS developed for port and maritime transport should focus on topics such as water quality, air quality, waste management, habitat conservation, noise, dredging, contaminated soils, anti-fouling paints and energy consumption. It is of absolute necessity to consider all relevant compliances with legislation affecting shipping and port operations [85]. An EMS is a formal system for proactively managing the environmental footprint of a port, providing a framework designed to achieve continual environmental improvement beyond regulatory compliance. It incorporates environmental considerations and decision-making into a port's day-to-day operations and into its strategic planning. An EMS has several benefits such as it integrates environmental efforts with business goals, increases sustainability, allows for more efficient use of resources, improves communication and promotes community awareness and support.

The management techniques available to port authorities to implement EMS include PERS-SDM designed and developed by EcoPorts Foundation and supported by Lloyd's Register and ISO 14001-EMAS. Nowadays there are a growing number of certified ports and terminal operations, as the port of Dover (that received the ISO 14001 certification in 2008), the port of Houston authority (the first US port to achieve ISO 14001), the Livorno port authority (in 2004 it gained ISO 14001 certification and was registered as an EMAS compliant organisation), the ports of Boston, Corpus Christi, Houston and Los Angeles (they have progressed to ISO 14001), the Virginia port authority (in 2008 it gained ISO 14001 certification), the Maryland port administration (it has implemented an EMS based on the ISO 14001-2004), the port of Portland (it is supported by an ISO 14001:2004 certified EMS) and the Belfast harbor (which is certified to the ISO 14001:2004 standard) [85]. During 2008, the ports of Rotterdam, Dublin, Peter Head and Alicante gained their first PERS certification.

Harbor managers are under increasing pressure to encompass environmental management within ports and harbors. Regulatory and management authorities must be aware of environmental thresholds and constraints while biogeophysicochemical environmental parameters can be a useful tool for the achievement of an effective maritime pollution management. The current work furnishes indicators based on environmental parameters to monitor and audit the effectiveness of EMS and EP in ports. It includes a critical evaluation of the parameters, an assessment of methods and techniques and guidelines for a maritime pollutants management. These indicators are powerful tools supporting sound decisions when developing, shaping and evaluating environmental management systems and policies. Also, they enable recommendation of remedial measures to improve environmental quality and the continual upgrading of environmental performance.

Table 5: International port authority website research.

Name	Country	Website	Main environmental actions
Africa			
National ports authority of South Africa	South Africa	www.transnetnationalports authority.net	– ISO 14001 – Identification of significant issues concerning waste – Air quality – Ecological inventories of plants, animals, other biota and habitats
Asia			
Singapore	Singapore	www.mpa.gov.sg	– Green service provider – seaport
Europe			
Aberdeen	United Kingdom	www.aberdeen-harbour.co.uk	– PERS certified – Dredging/waste/oil spills – Energy consumption monitoring – Air quality monitoring
Algeciras	Spain	www.apba.es	– Water, fuel and electricity consumption reporting – Carbon footprinting accounting – Waste recycling
Barcelona	Spain	www.apb.es	– Air quality monitoring
Cartagena	Spain	www.apc.es	– ISO 14001 – EMAS – Inventory of Env Aspects – Water, electricity and fuel consumtion reporting – Reporting of waste generated – Air quality monitoring
Cork	Ireland	www.portofcork.ie	– PERS certified – Procedure for bunkering notification – Noise monitoring – Dust monitoring – Environmental awareness training – Minimisation of oil spillage
Dover	United Kingdom	www.doverport.co.uk	– ISO 14001 certified – Marine Conservation Society in the Good Beach Guide Recognition – Monitoring of species diversity – Water quality analysis – Visual monitoring of vessel emissions – Recycling facilities across all working areas – Water, electricity, fuel consumption monitoring – Carbon footprint reporting
Felixstowe	United Kingdom	www.portoffelixstowe.co.uk	– PERS certified – Environmental aspects, impacts and performance – Carbon footprint reporting
Gijon	Spain	www.puertogijon.es	– ESPO Award 2009 – ISO 14001 – Air quality (PM_{10}) monitoring
Helsingborg	Sweden	www.port.helsingborg.se	– Combitermnal (logistics center) – County Administrative Board's environmental permit – Discount on the port tariffs for vessels with catalytic emission control
La Coruna	Spain	www.puertocoruna.com	– Waste recycling – Water quality and hydrological planning – Air quality

Table 5 (continued)

Name	Country	Website	Main environmental actions
Port of Poole	United Kingdom	www.phc.co.uk	– Noise – Carbon footprinting accounting – Water, fuel and electricity consumption reporting – Sustainable procurement policy – Carbon footprint reporting – Water usage reporting – Waste recycling reporting
Latin America			
Colonia	Uruguay	www.anp.com.uy	– Environmental policy – Environmental principles – Inventory of legislation
Montevideo	Uruguay	www.anp.com.uy	– Environmental policy – Environmental principles – Inventory of legislation – Environmental impact assessment – Guidelines for the management of Hazardous cargo
North America			
Colborne	Canada	www.seaway.ca	– Green marine certification – Ballast water management – Reducing greenhouse gas emissions – Icebreaking Study – Environmental Conformance Verification (ECV) Program – Threatened species and protected habitats
Los Angeles	USA	www.portoflosangeles.org	– Air quality monitoring – Alternative Maritime Power™ – Clean Air Action Plan – Environmental management system – Vessel Speed Reduction Program – Wildlife Habitat – Water and sediment quality improvement initiatives
Montreal	Canada	www.port-montreal.com	– Partner of the international Green Award Program – Green Marine certification
San Diego	USA	www.portofsandiego.org	– Cooper Reduction Program – Green Port Program – Clean Air Program – Water quality monitoring – Soil and sediment remediation – Storm Water Management Program – Hull Paint Study
Savannah	USA	www.gaports.com	– Environmental Policy – Emissions & Fuel Efficiency Study
Oceania			
Abbot point	Australia	www.nqbp.com.au	– Environmental Management Plan – Marine Environment – Water and sediment quality – Ambient air, noise, and weather monitoring
Brisbane	Australia	www.portbris.com.au	– Waste management – Water quality – Environmental Management Program (aspects and impacts, objectives and targets, EMS)

Table 5 (continued)

Name	Country	Website	Main environmental actions
Dampier	Australia	www.dpa.wa.gov.au	– Flora and fauna – Dredge materials – Identification of ecological values – Environmental management system – Physical water quality monitoring – Monitoring for potential contaminants in the stormwater drains – Rainfall monitoring
Esperance	Australia	www.esperanceport.com.au	– Environmental Management Plan – Dust, noise, sediment and weather monitoring
Geraldton	Australia	www.gpa.wa.gov.au	– Dust reduction strategy – Environmental Management Plan – Stormwater Monitoring Program – Wastewater Management Plan – Air Quality Monitoring Program
Melbourne	Australia	www.portofmelbourne.com	– Climate change strategy – Managing contaminated land – Water conservation – ISO 14001
Nelson	New Zealand	www.portnelson.co.nz	– ISO 14001 – Noise Management Plan – Fumigation – Dredging

5 Membership of sponsoring body

Membership of the IUPAC Chemistry and the Environment Division Committee for the period 2010–2011 was as follows: N.Senesi, L. McConnell, W. Peijnenburg, W. Cukrowska, P. Fedotov, S. Herve, N. Kandile, W. Kördel, K. Tanaka, P. Wine, M. Dassenakis, H. Garelick, L. Klasink, K. Racke, E. Tombácz, B. Xing, C. von Holst, I. Bhanger, M. Goodsite, G. Jiang, R. Koohana, N. Maňay, S. Safiullah, Y. Shevah, T-K. Soon, S. Tepavitcharova, M. Veber, P. Visoottiviseth.

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List of acronyms

AAS	Atomic absorption spectrometry
BOD	Biochemical oxygen demand
CFCs	Chlorofluorocarbons
CGC-ICP-MS	Inductively coupled plasma mass spectrometer as detector after capillary gas chromatography
DO	Dissolved oxygen
EMAS	Eco Management and audit scheme
EMS	Environmental management system
EP	Environmental policy
EPA	US Environmental Protection Agency
ESPO	European Sea Ports Organisation
GC	Gas chromatography

GC-ECD	Gas chromatography with electron capture detector
GC-FID	Gas chromatography – flame ionization detector
GC-ICP-MS	Gas chromatography-inductively coupled plasma mass spectrometry
GC–MS Gas	Chromatography coupled mass spectrometry
GFAA	Graphite furnace atomic absorption
HAP	Hazardous air pollutants
HCFCs	Hydrochlorofluorocarbons
HPLC	High performance liquid chromatography
HR GC-MS	High resolution gas chromatography – mass spectrometry
ICP-AES	Inductively coupled plasma atomic emission spectrometry
IDMS	Isotope dilution mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organization of Standardization
MPN	Most probable number
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PERS	Port Environmental Review System
PM	Particulate matter
POPs	Persistent organic pollutants
SDM	Self diagnosis method
TBT	Tributyltin
TPH	Total petroleum hydrocarbons
VOCs	Volatile organic compounds

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