



LIFE09 ENV/GR/000291

REACH Protocol for Emissions and Accident Scenarios in Supply
and Distribution of Fuels and Petrochemical products

*SUB ACTION 2.5 Detection methods for Hazardous Chemicals (HazChem)
emissions, leaks, spills and damage on air, soil and water*

*Review of industrial practices, BREFS in monitoring and quantifying emissions to
the environment.*

SUB ACTION 2.5

**Executive Summary of the Deliverable “Spill detection
methods and good practices” in English**



LIFE+ Environment Policy & Governance

Executive summary

In this deliverable a review of the existing detection methods and emission estimation techniques (EETs) in air, water and soil, as well as of the best industrial practices in monitoring and quantifying emissions, has been performed. Moreover, a review of past accidents regarding the transportation and storage of dangerous substances has been performed. The study performed under sub-action 2.5 included the analytical overview of:

- the most systematic detection methods and emission estimation techniques (quantification of emissions) used in industrial practices (according to EU and International standards);
- the most important substances frequently detected in case of releases of dangerous products to the environment;
- the main regulatory criteria and methods to detect pollutants with focus to petrochemical product releases and
- critical points for the detection of emissions in every life cycle (LC) stage of fuels.

The deliverable consists of four (4) Chapters where the procedures and detection methods of emissions and leaks/ spills on air, water and soil are recorded in detail, while in Chapter 4 the analysis of past accidents is presented.

Detection methods of emissions/ leaks on air (Chapter A)

In Chapter A air emission sources for the examined lifecycle stages of fuels and petrochemicals are identified and the pollutants per emission source in refineries and fuel facilities are recorded. Emissions from distribution terminals include mainly volatile organic compounds except for methane (NMVOCs). In the deliverable, are described analytically the emissions and are presented the emission estimation techniques regarding leaks from critical industrial equipment (pumps, valves, flanges, etc.), storage tanks, loading and transport of products via different means (tank trucks, trains, ships), as well as service stations' operation.

Fugitive emissions from critical equipment in refineries and industrial facilities in general, are the largest source of emissions of volatile organic compounds (VOCs). According to United States Environmental Protection Agency (EPA), the main sources of emissions of VOCs in refineries and industrial facilities in general are the valves and flanges as they constitute main components of the facilities' equipment and are usually present at the facilities in large numbers.

A series of best industrial practices and international standards that require implementation of a Leak Detection And Repair (LDAR) program is implemented for the detection and repair of leaks of volatile compounds from the equipment and the improvement of safe conditions in petroleum products facilities. The LDAR program is implemented to all possible sources of leaks of VOCs from equipment components, due to loss of tightness, while according to the requirements of EN 15446:2008 standard it includes all light petroleum products. In the deliverable analytical reference is made to the implementation framework and the elements comprising the LDAR program.

The EPA's method M21 “Determination of volatile compound leaks” is implemented for the identification of leaks using portable measuring instrument. In the deliverable analytical reference is made to the main techniques for quantification of emissions of VOCs according to EPA's guideline “Emission Estimation Protocol for Petroleum Refineries”, including emission correlation equations for the equipment measured based on measurement data and average emission factors for equipment components for which there are no measurement values. Moreover, detailed analysis is performed for emission estimation techniques and methods according to EPA and CONCAWE for the following: a) loading procedures (losses during tank truck, ship, rail vagon loading) taking into account the loading methods and the product being loaded, b) losses during transport with ships and barges, c) losses from service stations' operation and d) storage tanks (Tank Farm Fugitives).

Detection methods of emissions/ leaks on water (Chapter B)

In Chapter B, dangerous chemical substances for the environment with emphasis on the aquatic environment are recorded. In the framework of the project a review has been performed regarding past accidents with significant impacts to the environment. The dangerous substances involved in major accidents with significant impacts to the environment are: dangerous for the (aquatic) environment

substances as defined in SEVESO II Directive (R50, R50/53, R51/53), insecticides, herbicides and pesticides, petroleum products (e.g. gasoline, kerosene, diesel, fuel oil), substances used in firefighting and pyrolysis products, etc. Toxic combustion products such as SO₂, NO_x, Polycyclic Aromatic Hydrocarbons (PAHs), Persistent Organic Pollutants (POPs), etc. are recognised as compounds and by-products of the above mentioned products with significant impacts to the aquatic environment

In addition, priority substances in the field of water policy and allowable emission thresholds according to the Directive 2008/105/EC, as well as the properties of dangerous substances for the aquatic environment according to CLP Regulation and the Globally Harmonised System (GHS) for Classification and Labelling of Chemicals are recorded.

Regarding petroleum products, Petroleum Hydrocarbons, of which petroleum products are mainly composed of, are examined, with emphasis on Aliphatic Hydrocarbons and PAHs, and the origin of hydrocarbons is identified through the fingerprinting method. Moreover, emission limits regarding waste water of industrial facilities and petroleum products facilities, according to Ministerial Decision 50388/2704/E103/2003, are recorded.

Finally, the steps for identification of petroleum compounds in water samples, such as EPA's guidance for the preservation of samples, determination of Total Petroleum Hydrocarbons (TPH) and other petroleum compounds, analysis techniques (e.g. Gas chromatography (GC), Infrared spectroscopy (IR), Barometric method, enzyme immunoassay method) are described.

Detection methods of emissions/ leaks on soil (Chapter C)

In this chapter are described the categories of solid waste based on criteria and parameters as defined in Decision 2003/33/EC, and the threshold values of dangerous solid waste are defined. Sampling and analysis methods of solid samples based on European and International Standards are identified. The methods used include sampling, leaching tests, digestion of raw waste and analysis of solid samples.

Accident statistics (Chapter D)

In the framework of the project an accident analysis of ~ 25000 industrial accidents (of which ~ 900 involving LPG) and a review of past accidents, registered in databases, involving dangerous substances in transportation have been performed. The analysis showed that the most (safety) critical LC stages and HazChem transportation means per hazard class of dangerous substances can be identified based on the frequency of transportation and the consequences in case of an accident.

The main conclusions of the review show that:

- 50% of international accidents is related to road/ rail transport and loading/ unloading of the product, while 20% is related to pipelines.
- From ~ 900 recorded accidents involving LNG, 55% of these is related to road transport and loading/ unloading, while significant reduction of accidents is presented after the implementation of ADR Agreement in 1978.
- Over 85% of accidents with severe consequences is related to road transport and loading/ unloading.
- Products of hazard class 3 (flammable liquids) and of hazard class 2 (flammable and toxic gases) are involved in accidents with severe consequences at a percentage over 80%, while hazard class 8 (corrosive substances) at ~ 10% and hazard classes 5, 6 and 9 at 4%.
- For specific products, a hazard index (for fatalities and injuries) applied in a sample of ~ 6000 accidents with severe consequences (USDOT) for a five year period (2005-2009), showed that gasoline and diesel are involved at 85%, while chlorine, sulphuric acid and LPG, at 3%, 5% and 7% respectively.

The main environmental consequences of major accidents are mostly related to large volume releases of environmentally dangerous substances to the aquatic environment and take place in incidents with lower frequency of occurrence comparing to those that involve human casualties. Relatively small leaks of chemical substances (smaller than the lower thresholds that satisfy the requirements of SEVESO Directive) can cause significant environmental consequences, but this is not historically connected to petrochemical products. Substances with risk phrases R50, R50/53, R51 and R51/53 are involved in major accidents with environmental consequences. Hazard indexes applied to these cases should refer to the extent and type of consequences rather than the frequency of releases.