

European Center for Forest Fires (ECFF)

# Forest Fire Net

*Special issue with the Proceedings of the workshop:*

“Air-quality monitoring in the field  
and personal protective equipment  
in big forest fire incidents: a state-of-the art and beyond”

Paris, 12-13 of December 2005

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## ***Prologue***

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Forest fires are physical or man-made disasters with environmental, social and economical consequences. Forest fire smoke in big forest fire incidents, such as those that have occurred in South Europe, in S.E. Asia and other areas, poses not only a threat, but also a “challenge” for improving air-quality monitoring in emergency situations, for enhancing personal protection means and for developing advanced early warning systems.

The Paris workshop was organized within the framework of the EUR-OPA Major Hazards Agreement of the Council of Europe. It was entitled: “Air-quality monitoring in the field and personal protective equipment in big forest fire incidents: a state-of-the art and beyond”. It will definitely carry a wealth of knowledge, both scientifically based and operationally acquired. The workshop was meant to be a sampler of cutting-edge technologies for air-quality monitoring in emergency situations and will play a central role in further elaborating the results of the teleconference “Short and long term health impacts of forest fire smoke on the fire-fighters and the exposed population”, which was previously organized by the European Center for Forest Fires (see FFNet Vol 3, October 2005). The Teleconference focused on the issues of the toxicology of forest fire smoke, means of personal protection for personnel and population, development of indexes for air-quality monitoring and evacuation criteria.

Coping with all issues of forest fire smoke seems to be a specialized issue, but it is not; it is both a core disaster discipline and a key methodology that can be applied on other disasters and threats, such as chemical accidents and deliberate release of chemical, radiological and biological agents. It is also a key element in developing reliable early warning systems.

More specifically, air-quality monitoring in emergency situations, or as a part of an early warning system, includes sampling and detection equipment and also data analysis. Air-quality monitoring in those situations must ensure reliability and effectiveness. Selection of the right type of monitoring systems, correct positioning, proper maintenance and correct calibration are necessary for managing an effective response.

If we consider where relevant organizations and the Centers of the Agreement stand today, in terms of understanding and managing forest fire smoke issues, we are faced with scientific, operational, technical and organizational challenges. A response to those challenges has various difficulties, such as obtaining enough resources, persuading in using multidisciplinary approaches, finding out how to use already existing knowledge, insisting on carrying out further research on relevant areas, developing and testing early warning systems and preparing emergency plans.

Milt Statheropoulos  
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## ***Opening Session***

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### **➤ Opening address**

***(E. Fernandez-Galiano, Council of Europe)***

I am pleased to welcome you to the workshop “Air-quality monitoring in the field and personal protective equipment in big forest fire incidents: a state-of-the art and beyond”, organized within the framework of the EUR-OPA Major Hazards Agreement of the Council of Europe, in cooperation with European Center for Forest Fires (ECFF). In the framework of the Agreement, we support the development of the technical and scientific work of the Centers, as an important contribution to the fulfillment of its political objectives of providing more safety for citizens and preparing them to better cope with natural and technological hazards. We aim at turning the Centers in living centers of knowledge on risk issues and useful tools, both for the States and the populations concerned, which will benefit from the work of the Centers in many different ways. Forest fires are becoming one of the main security concerns of many states of Europe, not only for their economic and environmental impact, but also for the impact that smoke from forest fires have on health. In a context of climatic change, forest fires will certainly increase affecting more severely our natural heritage and the livelihood of many rural areas. It is important that the knowledge gained in the effects of forest fires becomes better publicized. One of the priorities of the Agreement is the dissemination of results of the work in the field of major natural and technological disasters, carried out by the Centers. This is the reason we took the initiative for co-organizing this workshop. We hope that the workshop will facilitate cooperation and knowledge exchange and will better define the activities of the Agreement in the particular field of forest fires, on European and International level.

I am looking forward to a successful workshop.

Eladio Fernandez-Galiano

Executive Secretary of the European  
and Mediterranean Major Hazards  
Agreement (EUR-OPA)

## ***Session 1: On-line monitoring methods in the field and early detection systems of forest fire smoke***

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This session includes presentations referring to state-of-the art methods and techniques, which are used for the on-line monitoring in the field. A number of field analytical instruments, such as roving GC-MS (Gas Chromatography-Mass Spectrometry), GC/GC (Gas Chromatography – Gas Chromatography) and IMS (Ion Mobility Spectrometry) are presented and also their possible advantages compared to traditional methods are discussed. In addition, new trends regarding air-quality monitoring, such as miniaturization of instruments, with the purpose of preparing wearable instruments, are described. Moreover, systems for early detection of smoke are presented. An introduction to the session is given, with emphasis on the specifications of field instruments.

### **➤ Instrumentation for field monitoring in forest fires**

***(M. Statheropoulos, European Center for Forest Fires, S. Karma and E. Katsou, National Technical University of Athens, Gr)***

#### **1. Introduction**

The purpose of this work is to discuss methods and possible instruments' specifications for air-quality monitoring in a forest fire incident. The chemical composition of forest fire smoke (ffs) and the types of field instruments are given. The possible requirements for the ffs field monitoring are presented. Specifications of field instruments for air-quality monitoring in a forest fire are defined by field requirements and also the need to monitor human exposure.

#### **2. Chemical composition of forest fire smoke**

Forest fire smoke (ffs) is a complex mixture of gases, liquids and solids. In a more operational view, ffs can be considered as a complex mixture, originated from the combustion of forest fuels and also the combustion of other materials co-burned, as the flame-front expands. Possible scenarios of forest flame-front expansion and the related ffs chemical composition can be integrated in a road-map for air-quality assessment (M. Statheropoulos and S.Karma, FFNet, 3 (2005) 6).

### 3. Air-quality monitoring in the field

#### 3.1. Types of field monitoring

The following types of field analysis can be used:

- In-situ.
- On-site.
- On-line.

#### 3.2. Classification of field instruments in general

Depending on the size, the weight, the use and the motion, field instruments can be classified as:

- Portable instruments (hand-held).
- Mobile labs (units, roving systems).
- Wearable instruments.

#### 3.3. Field instruments that can be used in a forest fire incident

##### 3.3.1. Hand-held

- *Portable instruments* (e.g. CO, CO<sub>2</sub> and other sensors, particle analyzer, PID analyzer, GC-MS, GC-IMS, GC-GC).



Figure 1. CO/CO<sub>2</sub> sensor.

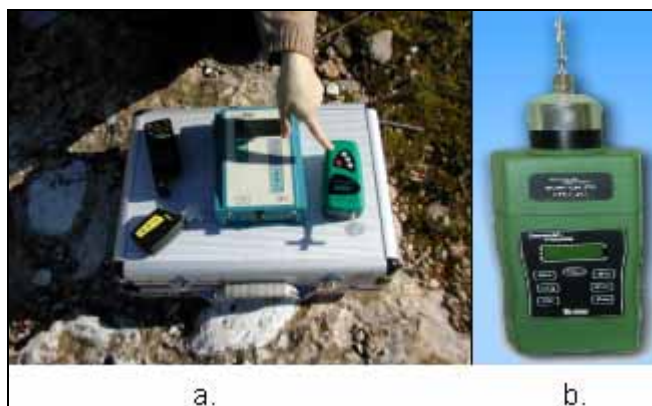


Figure 2. Particle analyzer (a) and PID analyzer (b).



Figure 3. GC-IMS (a) and field portable GC-MS (b).

- Miniaturized instruments (e.g. IMS).
- Hand-held field luggage (e.g. UV, MS, GC-MS).



Figure 4. Miniaturized IMS (a) and a Hand-held field luggage (b).

### 3.3.2. Mobile labs

#### a. Mobile units

- Laser based instruments.
  - LIDAR (Light Detection And Ranging technique) is a method for air-quality monitoring from a distance. It has been used for air pollution applications and also the recent years for smoke detection in a forest fire (A. Sapkota et al., Environ. Sci. Technol., 39 (2005) 24).
  - TOF-MS (Time-of-Flight Mass Spectrometry) has recently been used for single particle size and composition measurements, in the size range of 30 to 3000 nanometers, as an Aerosol -TOF-MS instrument (TSI).
- FTIR (Fourier Transform Infrared Spectroscopy), has been used for spectroscopic sensing in the field of NH<sub>3</sub> emissions, in a pine forest fire, where trees treated with retardant were burned (F.T. Kantrowitz et al., Atmos. Environ., 29 (1995) 3303).

#### b. Roving Systems

- Roving GC-MS system has been used for mapping emissions' concentrations in an area (H.L.C. Meuzelaar, Field Anal. Chem. Tech., 1 (1996) 109); it will be thoroughly described in a following presentation.

### 3.3.3. Wearable

Wearable instruments can be integrated to the uniform of the operator, e.g. miniaturized ion mobility system (IMS).

## 4. Special characteristics of ffs monitoring

In a forest fire:

- Dynamic phenomena usually take place (e.g. turbulence is observed compared to laminar flows).
- Very rapid changes of concentration profiles in space and time occur (periodicity is possible but with no constant period).
- The environment is considered “heavy” (soot, tars, high temperatures and humidity) and hostile, not only for the operator but also for the reliable operation of the instruments.

## **5.Human exposure to ffs**

Exposure to forest fire smoke (ffs) can be quantified as the concentration of the smoke components in the subject in contact, integrated over the time duration of that contact. In order to have a more representative assessment of ffs health impacts, the following should be considered:

- Exposure to ffs is simultaneous exposure to multiple substances, such as gases, liquids, solids (mixed exposure).
- A potential synergism may exist among various ffs components.
- Exposure limits to ffs components need to be established, taking into consideration that ffs exposure is taking place in the field, compared to occupational indoor exposure.

Consequently, there is a need for on-line monitoring of a broad range of pollutants simultaneously, in order to assess exposure to ffs.

### **5.1.Exposure assessment**

Exposure assessment to hazardous compounds, originated from various sources, (e.g. forest fire, urban air pollution, indoor pollution, chemical accident etc.), can be carried out by using:

- Biomarkers in urine samples for wood smoke exposure, (e.g. family of methoxylated phenols, levoglucosan) (EPA NW Research Center for Particulate Air Pollution and Health, Year 3 Progress Report, June 2001 - May 2002, August 20, 2002; EPA NW Research Center for Particulate Air Pollution and Health, Year 4 Progress Report June 2002 - May 2003, June 12, 2003).
- VOCs in expired air, such as BTX, styrene or other exogenous compounds, as indicators of fire-fighters exposure to smoke (A. Georgiadou, A. Agapiou and S. Karma, FFNet, 3 (2005) 17).
- VOCs, which are characterized potential carcinogens, (e.g. Butadiene-1,3 or PAHs, e.g. Benzopyrene), measured in personal exposure samples (MATCH project).
- Models, which use various properties, (e.g. Henry's law constant, chemical's octanol-water partition coefficient, organic carbon sorption coefficient of compounds), as tools for estimation of human and environmental exposure to chemicals (Chem. Eng. News 3 April, 84 (2006) 32).

- Empirical approaches:

Various empirical approaches have been proposed in the literature:

*a) Calculating the assessment criterion  $E_m$  for mixed exposure*

According to the equation (1), the mixed exposure assessment of fire-fighters due to their exposure to ffs complex mixture, has been done by calculating the assessment criterion  $E_m$ :

$$E_m = C_1/T_1 + C_2/T_2 + \dots + C_i/T_i \dots + C_n/T_n \quad (1),$$

where,  $C_i$  represents concentrations of the respective substances and  $T_i$  represents the threshold limit value of the respective substances (American Conference of Governmental Industrial Hygienists, ACGIH). According to this approach, values of  $E_m$  more than 1 are considered critical (Morioka et al., Arch. Environ. Health, 54 (1999) 341). This empirical approach was used to estimate  $E_m$  values for fire-fighters during their work-shift for substances, such as acrolein, formaldehyde and respirable particulate ( $PM_{3.5}$ ), by using the ACGIH TLVs as divisors in the equation (1) (Reinhardt et al., Res. Pap. PNW - RP - 526, 2000).

*b) CFK equation for estimating Carboxy-hemoglobin (COHb) in blood*

Another empirical approach is the use of CFK (Coburn, Foster, Kane) equation. Inhalation of CO increases production of Carboxy-hemoglobin (COHb) in blood, whose concentration in normal levels is about 5%. If concentration level of COHb exceeds 5%, then various symptoms can be recorded (tissues hypoxia that causes headache, dizziness, nausea). The CFK equation takes into consideration variables, such as the duration of exposure, lung ventilation rate, rate of endogenous CO production, diffusion rates in the lung, blood volume, barometric pressure and partial pressure of CO and oxygen in the lung. CFK equation does not take into account the effects of altitude on CO exposure and COHb levels. NIOSH recommends that when exposures to forest fire smoke occur at altitudes above 5000 feet, then the loss of the oxygen-carrying capacity of the blood should be taken into consideration (Reh et al., Health Hazard Evaluation Report No. 88-320-2176, 1992, [Wyoming http://www.cdc.gov/niosh/hhe/reports](http://www.cdc.gov/niosh/hhe/reports)).

*c) Calculation of exposure limit reduction factor in non-traditional work-shifts*

To evaluate compliance of non-traditional work-shifts with 8-hour PELs, OSHA uses simple formulas to calculate an exposure limit reduction factor. For estimating exposure limits for various compounds, an empirical model has been proposed. Equation (2) shows the recommended model by OSHA. Exposure limits for acrolein and  $PM_{3.5}$  are based on acute irritant effects and do not need to be adjusted

downward for longer work-shifts. For the CO, exposure limit calculation is based on acute toxic systemic effects and thus, adjustment is necessary for longer duration work-shifts. Equation (2), is used to calculate CO exposure during an extended work-shift:

$$\text{Adjusted CO exposure limit} = \text{PEL} \times \frac{8}{\text{Duration}} \quad (2)$$

where, Adjusted CO exposure limit = the revised exposure limit to account for the extended work-shift,

PEL = the permissible exposure limit (or other exposure limit, such as the TLV) and Duration = the duration of the extended work-shift (hours) (Reinhardt et al., Res. Pap. PNW - RP – 526, 2000).

*d) Calculation of Time-Weighted Average (TWA) exposures*

In order to estimate the Time-Weighted Average (TWA) exposures of fire-fighters over the duration of a work-shift and while on the front-line, another empirical model has been proposed:

$$\text{TWA} = \frac{C_1 \times T_1 + C_2 \times T_2 + \dots + C_n \times T_n}{T_1 + T_2 + \dots + T_n} \quad (3)$$

where, T<sub>n</sub> = the time in minutes of period n, and C<sub>n</sub> = the pollutant concentration during period n (Reinhardt et al., Res. Pap. PNW - RP - 526, 2000).

**5.2.Methods for monitoring personal exposure**

A number of methods have been used for monitoring personal exposure. Among them, a “Personal Exposure briefcase” and a “Micro- Environmental (ME) box” (S. Vardoulakis et al., Measurement and modeling of exposure to air toxic concentrations for Health Effect Studies: MATCH) are included, as well as, more traditional approaches, such as collecting air-samples cartridges for later analysis in the lab.

It has been referred to the literature a method for measuring in personal breathing zone, by using diffusion dosimeters with the principle of gradient analysis, such as the drager long-term diffusion tubes (C.M. Reh and S.D. Deitchman, U.S. Department of the Interior National Park Service, Health Hazard Evaluation report,



No88-320-2176, NIOSH, 1992). Diffusive sampling, for simultaneous identification of a number of chemical substances (VOCs) and diffusive sampling of BTEX by a SPME method have also been reported (Podium 127, Papers 211-222, 2004 [www.aiha.org/abs04/po127.htm](http://www.aiha.org/abs04/po127.htm) - 25k).

FTIR (Fourier Transform Infrared Spectroscopy), solid-sorbent sampling and thermal desorption have also been used for chemical agent detection (Podium 127, Detection, Papers 211-222, 2004, [www.aiha.org/abs04/po127.htm](http://www.aiha.org/abs04/po127.htm) - 25k).

A method that is based on breath air analysis has been preliminary tested (A. Georgiadou, A. Agapiou and S. Karma, FFNet, 3 (2005) 17). The method is based on using Tedlar bags for collection of expired air samples of the subjects, who were exposed to smoke; samples were transferred into multi-bed sorbent tubes and analyzed by a TDU-GC-MS (Thermal Desorption- Gas Chromatography-Mass Spectrometry) instrument. The Volatile Organic Compounds (VOCs) determined consisted of products of several metabolic pathways (endogenous compounds) and the inhaled contaminants (exogenous compounds).

## **6.Specifications of instruments for air-quality monitoring in a forest fire**

In addition to the basic specifications of field instruments: selectivity, resolution, sensitivity, detection limits, precision and accuracy, size and weight, power consumption and maintenance requirements, speed, ruggedness and simplicity of operation, specifications are determined by the specific conditions of a forest fire.

Ideally, field instruments applied on air-quality monitoring in a forest fire should have:

- The ability to analyze a broad range of types of compounds.
- The ability to determine a broad range of concentrations, e.g. concentration may range from low to very high in different sites (space).
- The ability to measure in non-laminar air conditions (turbulence).
- Dynamic response in concentration changes (time).
- Minimum instrument contamination, without loss of compounds of interest.
- Minimum false alarms and cross sensitivity.
- Ability to measure human exposure.

➤ **Considerations for field portable hyphenated analytical instrumentation**  
(N.S. Arnold, FemtoScan Corporation and H.L.C. Meuzelaar, Institute for Combustion and Environmental Studies, University of Utah, Salt Lake City, UT, USA)

## 1. Introduction

Sampling in the field for air-quality monitoring has special characteristics. It occasionally needs fast moving, quick detection at ultra-low concentrations, high-speed separation, separation of complex mixtures (e.g. separation of forest fire smoke) and real-time data processing, in order to address effectively emergency plans needs. Instruments' hyphenation provides a number of advantages regarding the field needs described above, such as fast analysis and specificity.

### 1.1. Hyphenation benefits for field portable instruments

The benefits of hyphenation for field portable instruments are shown in Figure 1. Complicated mixture analysis in the field, using GC-MS, GC-IMS and GC-GC is a hyphenation application, which provides automation, unattended separation and extraordinary performance.

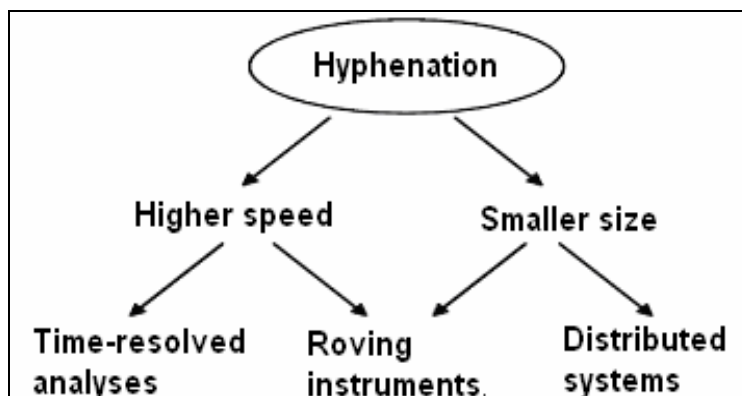


Figure 1. Dendrogram of hyphenation benefits of field portable instruments.

### 1.2. Why is hyphenation so powerful?

Figure 2, illustrates three hypothetical separation scenarios. The first scenario is a single separation using standard instruments, such as a gas chromatography instrument. The second scenario shows two independent separations of the same mixture of “chemicals.” This case can be thought as a separation of the same chemical mixture on two parallel GC columns with unique stationary phases. The third scenario shows the power of hyphenating the two separations. In this case, the

effluent peaks from one separation are immediately separated further in the second process. The ability to correlate two or more separations, provides geometric improvements in resolution or dramatic improvements in speed, so that hyphenation of instruments in harsh environments (e.g. field and process) is preferred. Specifically, the model of using hyphenation in order to increase specificity from an existing resolution separation can also be used in “reverse” to reduce instrument size, cost, or analysis time. This involves hyphenating lower-resolution separations to reduce the requirements of the individual separations, without decreasing overall performance of the analytical system. This approach is particularly important in response-time critical applications, such as the detection of highly toxic vapors (N.S. Arnold et al., *Field Anal. Chem. Tech.*, 4 (2000) 219).

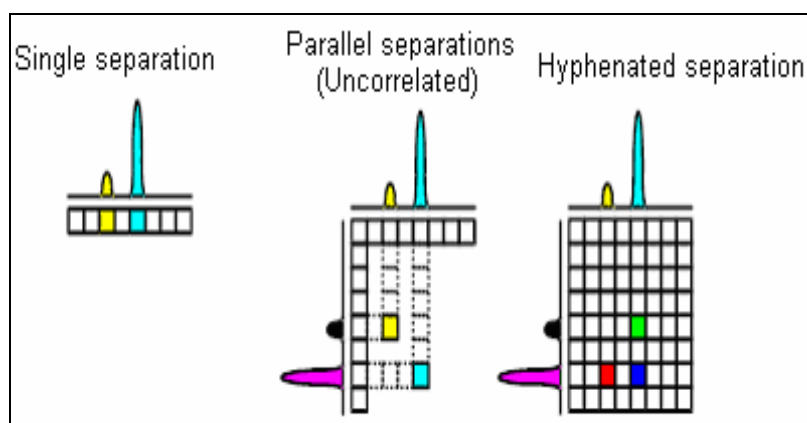


Figure 2. Resolution data resulted from single, parallel and hyphenated separation.

### 1.3.Theoretical GC concepts

Doubling the speed or the resolution of a single separation can have a tremendous cost in analytical performance according to the equations below:

- **Resolution:**  $R_s \approx \sqrt{N} \approx \left[ \frac{P_i}{D_{m,i}} \right]^{1/2} r$

- **Analysis Time:**  $t_r \approx \frac{N^2}{P_i} \approx \frac{R_s^4}{P_i}$

- **Detector flow:**  $\frac{dV}{dt_{srp}} \approx D_{m,i} r$

where, N is the number of theoretical plates of the GC column (limited for a given column radius),  $p_i$  is the column inlet pressure,  $D_{m,i}$  is the binary gas diffusion

coefficient of a component in the mobile phase at the column inlet pressure and  $r$  is the column radius.

## 2. Hyphenated instruments

### 2.1. Roving GC/MS

In Figure 3, a roving GC-MS system is presented. The GC-MS instrument is mounted on an electric-powered truck, in order not to have background interference from the exhaust emissions of the truck.



*Figure 3. Roving GC/MS instrument mounted on the bed of an electric-powered truck.*

In Figures 4 and 5, the block diagram of the Roving GC/MS instrument and its photograph are presented, respectively. This instrument utilizes an Enviroprobe device for direct atmospheric vapor sampling and a rapid TLGC (Transfer Line Gas Chromatography) separation of chemical species. More specifically, the sampling inlet is a flexible, heated sampling probe that leads to the AVS-TLGC module (Automated Vapor Sampling - Transfer Line Gas Chromatography). The main compartments are the MSD (Mass Spectrometry Detector) vacuum manifold, the turbo-molecular pump section, the molecular drag pump section, the oil-less membrane pump section and pump control switch and the quadrupole. MSD electronics consist of an ac switch, a dc/ac inverter and a buffer battery. The batteries are 12 V dc (min 100 Ahr  $\approx$ 4 field hours and max 200 Ahr  $\approx$ 10 field hours). The system also consists of a notebook PC and display (PCMCIA Cards), as well as, a carrier gas cylinder.

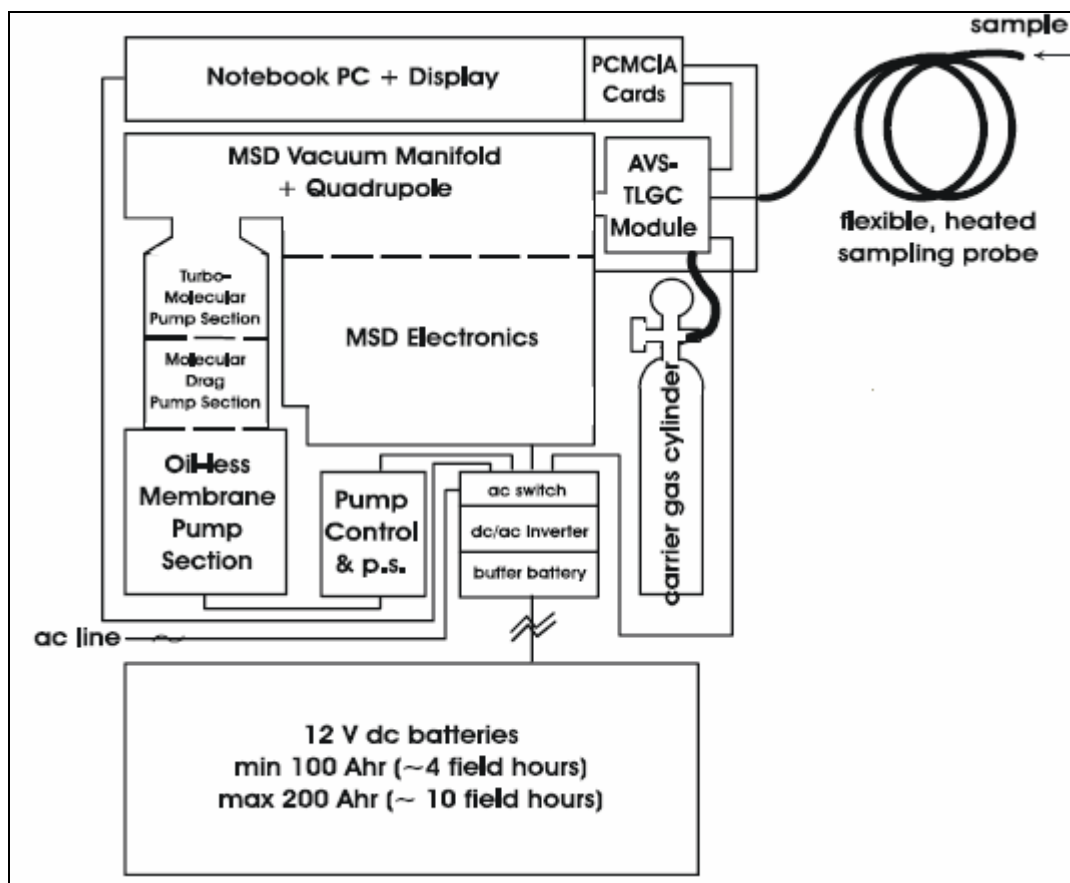


Figure 4. Block diagram of the roving GC-MS instrument.



Figure 5. Roving GC-MS instrument.

### 2.1.1.AVS-TLGC configurations

The complete AVS-TLGC (Automated Vapor Sampling-Transfer Line Gas Chromatography) system shown in Figure 6, is a small fraction of the MS size, but adds enormous analytical benefits. The AVS inlet in Figure 7 provides a valve-less coupling into Transfer Line Gas Chromatography (TLGC) for a high-speed pre-separation of analytes. This automated sampling device provides enough rationale for the use of the TLGC approach, where sampling is introduced onto the head of the column, without the use of intervening valves or seals. Therefore, in a typical TLGC/MS application the pressure drop is determined solely, by the vacuum in the MS housing and atmospheric pressure at the inlet.

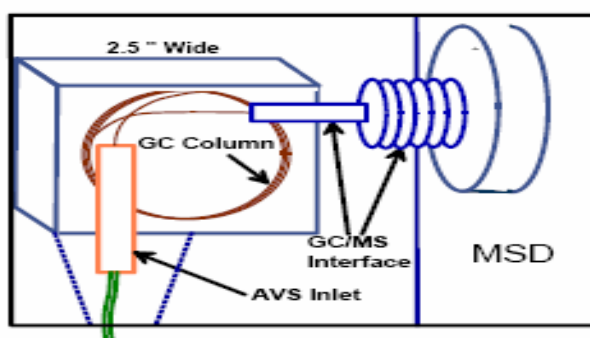


Figure 6. AVS (Automated Vapor Sampling), inlet coupling to a TLGC (Transfer Line Gas Chromatography) diagram.

This sampling approach reduces a number of potential sites for analyte condensation and sample loss and is consistent with doing near real-time GC (N.S. Arnold et al., *Field Anal. Chem. Tech.*, 4 (2000) 219).

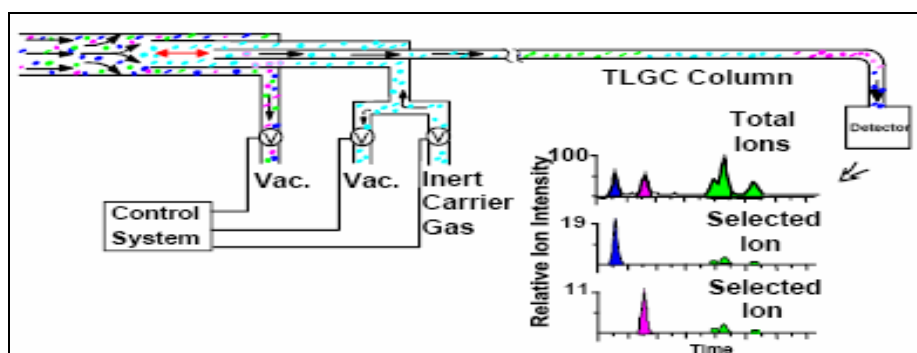


Figure 7. Diagram of valveness coupling of the AVS into TLGC, for high-speed pre-separation of analytes.

### 2.1.2. Anticipated performance of TLGC

Theoretical models allow prediction of GC separation and flow characteristics under fixed pressure drop conditions, as shown in Figure 8.

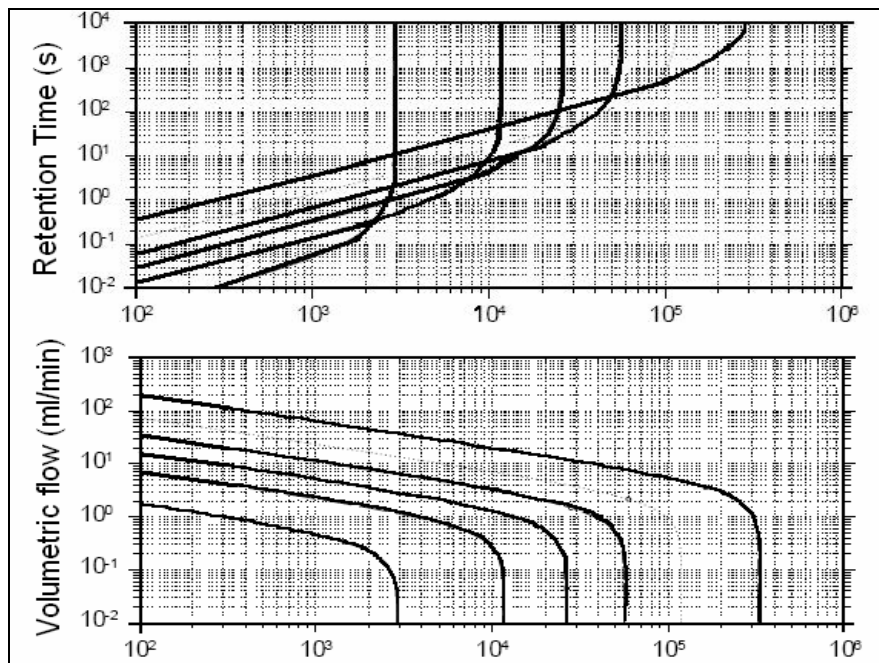


Figure 8. Theoretical diagrams to predict GC separation (theoretical plates) and volumetric flow characteristics, under fixed drop conditions (specific retention time).

### 2.1.3. High speed separations

Figure 9, illustrates the successive and rapid separation and detection of four simulants, which in fact is a mixture of four phosphonate compounds, by using a modified commercial instrument (roving GC-MS). The separation of the compounds is shown as graphs of relative intensity, plotted versus time. The compounds are intended to simulate the detection of Chemical-Weapons (CW) in the presence of interfering compounds. For each target compound a selection that is characteristic of the compound is used to illustrate the detection. The asterisks indicate a noise artifact, caused by the pressure pulse when the air sample is introduced. However, in this case, full mass spectras are being taken at four scans per second to confirm the detection of the target compound in a two-dimensional data space. In this case, all four compounds can be detected within 6 s of the corresponding vapor injection. This process can be rapidly repeated to track levels in near real-time.

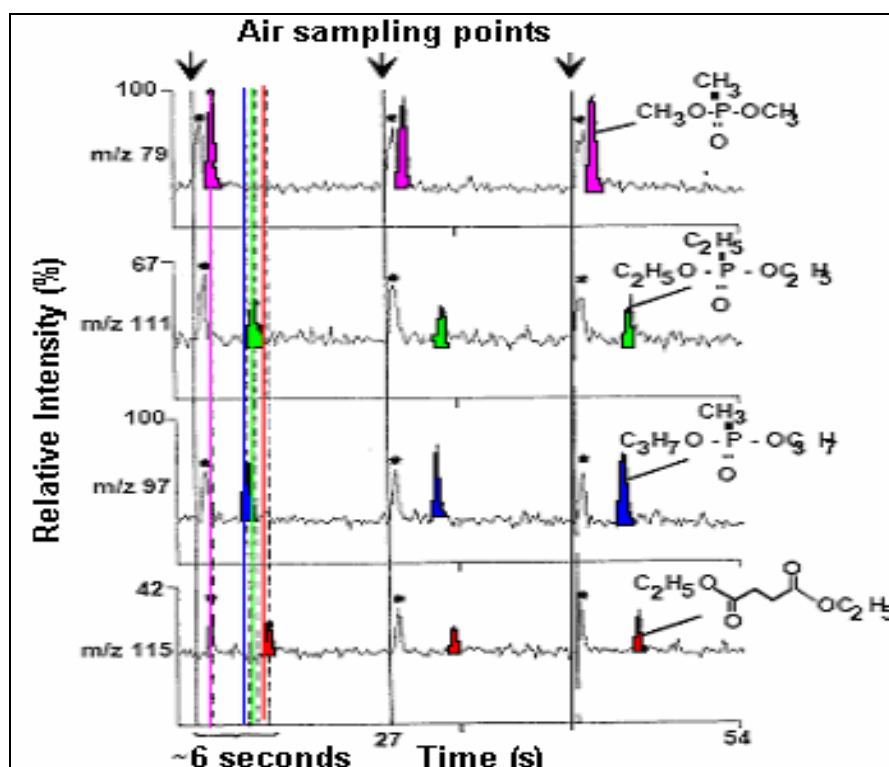


Figure 9. Successive separations of four simulants (relative intensity plotted versus time), introduced as a headspace mixture, by using the roving GC/MS instrument.

## 2.2. Application scenarios

GC-MS roving system can be used for evaluation of Point/Distributed Source Emissions, as presented in Figure 10.

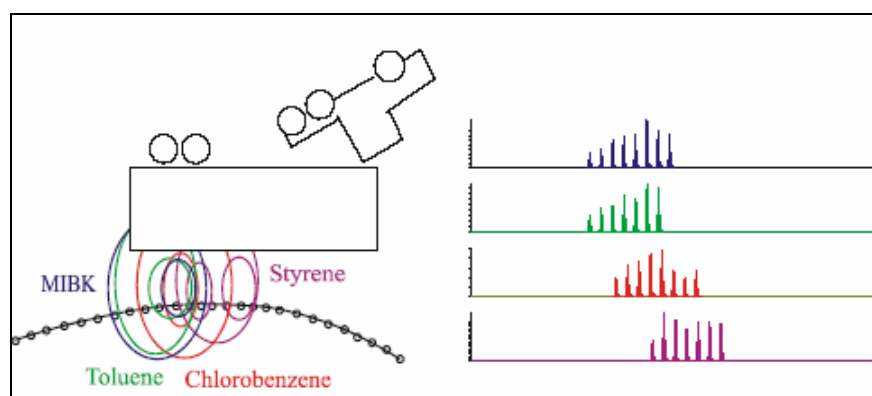


Figure 10. GC/MS roving system for evaluation of point/distributed source emissions.



### 2.2.1. Mapping emissions

“Roving” through the area gives real-time emissions data and makes possible the mapping of the emissions. In Figure 11, mapping of toluene concentration gradient (2 to 150 ppm) in a mildly shifting breeze, by the roving GC/MS system, is presented. Moreover, the relative ion chromatogram (RIC) of mass 91, used to monitor toluene, resulted from 150 repetitive GC/MS analysis in a period of 15 min, is shown.

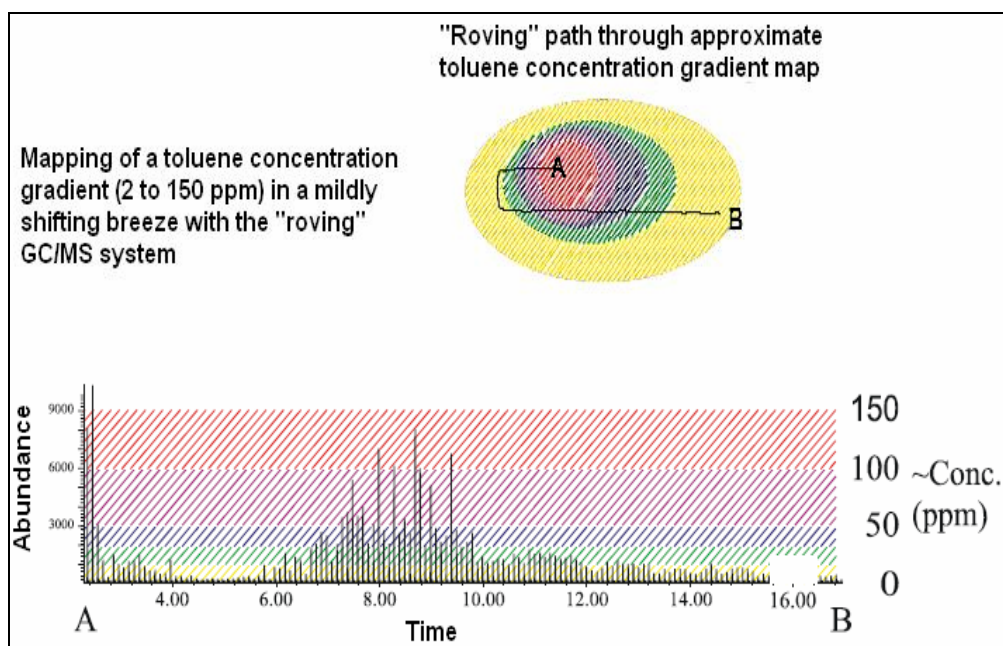


Figure 11. Mapping of toluene ( $m/z$  91) and relative ion chromatogram from 150 repetitive GC/MS analysis, in a period of 15 min.

### 3. Prototype hand-portable GC/IMS

A breadboard AVS-TLGC/Mini-IMS instrument was constructed, using an AVS device, an ambient-temperature GC column and a GI-Mini (Grasebylonics, Watford, UK) personal IMS device (see Figure 12). The AVS device of his system was constructed by using laboratory fittings and valves. These elements, along with additional plumbing and flow control electronics, were mounted on a wooden board for easy adjustment and modification. The electronics allowed for precise control of sampling times and monitoring of the pressure in the IMS cell. In this system, a modification of the IMS cell allowed the cell to be operated with a continuous flow through the cell, which is normally pumped only by diffusion in order to reduce the effective dead volume of the detector. This breadboard is operated in a fully re-

circulating mode; the air previously introduced into the unit via the sampling system, is either vented to atmosphere or scrubbed with molecular sieves, in order to be re-used as carrier gas for the GC system. This setup is similar to the approach used in previous hand-portable AVS-TLGC/IMS development efforts. Like this previously described instrument, the inlet is operated at ambient pressure, while the detector is operated at reduced pressure, driving the analyte and carrier gas through the column to the detector, in a fashion analogous to the roving GC/MS instrument.



Figure 12. Breadboard Hand-portable AVS-TLGC/IMS instrument (Prototype).

### 3.1. Direct IMS mixture spectrum

One of the most important issues limiting the application of IMS as a technique in field analytical chemistry is the non-linearity of the response. This non-linearity can be seen both in terms of calibration of individual compounds (linearity is typically less than three orders of magnitude) and in terms of different chemical responses suppressing each other. Figure 13, shows the effect of simultaneously exposure of a three phosphonates mixture to the IMS detector. This mixture contains dimethyl-methyl phosphonate (DMMP), diethyl ethyl phosphonate (DEMP), diisopropyl methyl phosphonate (DIMP) and diethyl malonate (DEM). As shown above, IMS response to the mixture provides a non-linear combination of peaks (13.a), while even a small amount of GC separation can be used to obtain unambiguous identifications (13.b–13.d). In general, the theory of hyphenated separations requires separations, where the response to a mixture of compounds is a linear combination of the responses to individual constituent compounds. Although there is a difficulty to quantitate the analytical improvements that might be anticipated from hyphenating non-linear techniques, improvements may still be anticipated. At the most basic level, a simple pre-separation of the target analytes already offers improved specificity, if the non-

linear separation technique provides unique chemical signatures (this is often the way that a laboratory GC/MS is operated, by using complete, baseline GC separations of the target analytes that are simply confirmed with the use of the MS spectra).

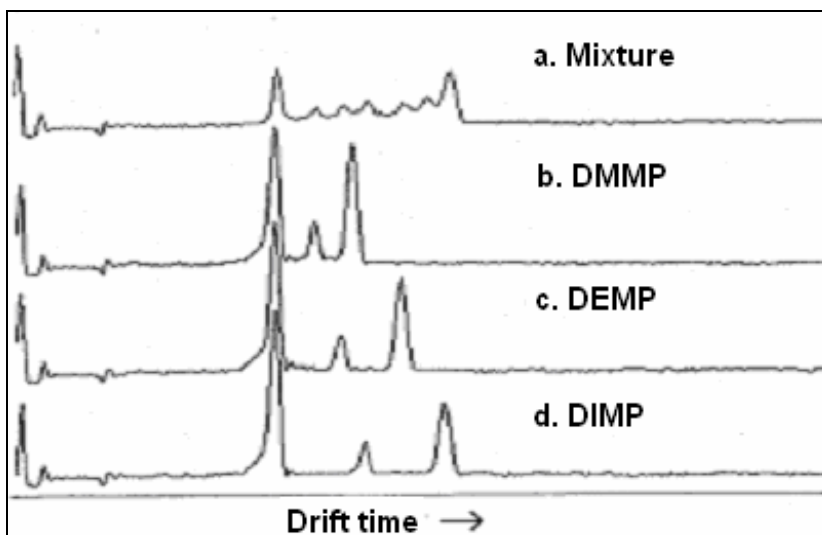


Figure 13. IMS response to a mixture of three phosphonate simulants.

### 3.2. Hyphenated GC/IMS separation

The individual compound spectra shown in Figure 14 are actually obtained at the center of the GC peaks, separated under the same conditions, as those shown in Figure 13. In this case, a mixture of three phosphonates, dimethyl methyl phosphonate (DMMP), diethyl methyl phosphonate (DEMP) and diisopropyl methyl phosphonate (DIMP), are separated in under 30 s to provide complete separation of the individual IMS spectra. This degree of separation mitigates the non-linearity of the IMS itself, by reducing the likelihood that interfering chemicals will alter the response of the system to a target chemical. The first sample is at the top of the Figure. The false colors in Figure 14 indicate signal intensity.

This approach illustrates that not all of the benefits of hyphenation require fully linear separations or, as will be shown below, fully linearly independent separation dimensions. The selection of reagent gas, which is used as a filter to select target analytes from potential interferants, is one of the most daunting tasks of IMS method development. Hyphenation can simplify this process and can be compatible with the simultaneous use of alternate reagent gases.

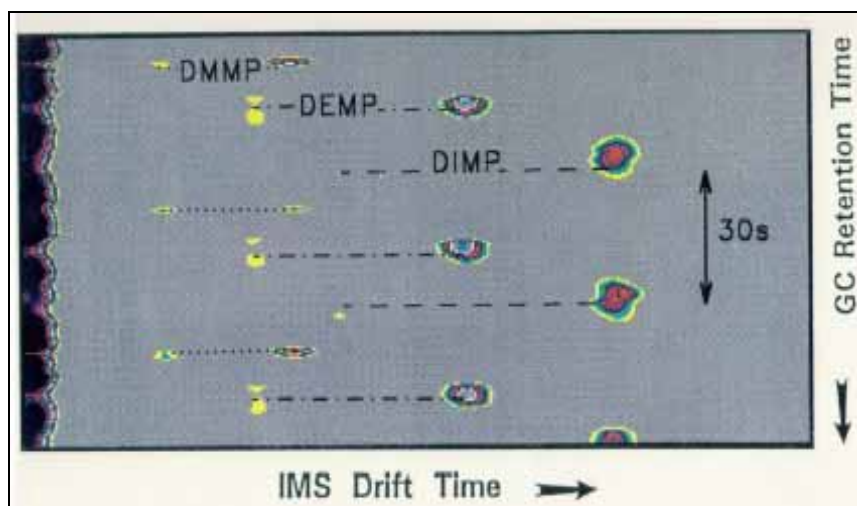


Figure 14. GC/IMS separation data for three phosphonate simulants.

The selection of the GC column for the IMS is somewhat different than the process associated with the MS. This difference is because the IMS detector is not operated under vacuum. Vacuum outlet conditions produce optimal separations in terms of both minimum plate height and number of plates per unit time.

#### 4. Portable GC/GC (/MS)

GC/GC portable instrument can be used in conjunction with an MSD (GC/GC/MS). It is worth noting that this system is quite portable, even though the MSD is relatively large and can be compared favorably with some portable GC systems in terms of weight and power requirements. Nevertheless, the only real rationale for using the MSD system, except for its availability and its nearly universal detection capability, is that it does not require the refitting of an ambient pressure detector for sub-ambient pressure operation. In practice, nothing in this GC/GC configuration precludes its use with any GC detector that is suitable for sub-ambient pressure operation.

GC/GC is based on a previous version of the roving GC/MS system described above. However, it is modified by the addition of a second “homemade” AVS-TLGC module to the system and the operation of the MS as a nonspecific chemical detector. Conceptually, this instrument is illustrated in Figure 15.

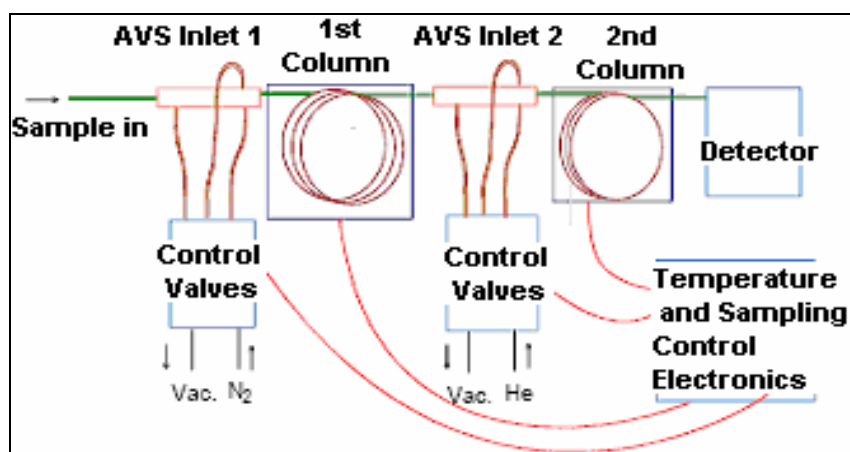


Figure 15. Schematic presentation of the breadboard vapor sampling GC/GC detector instrument.

Vapors are periodically introduced into the first AVS system. The AVS inlet configuration is slightly modified when the AVS/TLGC system is used for the second stage of GC/GC applications. Two modifications are necessary for introducing the sample into the second column. Firstly, the TLGC column, which provides the first stage separation, is effectively treated as the outer tube of the inlet. It provides a continuous flow of a gas into the second inlet, so that the first column effluent can periodically be injected into the second column. Secondly, the second sampling device must be maintained at a constant, sub-ambient pressure, by ensuring that the net flow through the device during the switching of the flows remains constant.

#### 4.1. Single detector time profile for GC/GC separation

Figure 16, illustrates how the data are acquired for a GC/GC instrument. There is only one detector at the end of the second column in this configuration (see Figure 15). The signal is a single trace that must be rastered to illuminate the 2-D nature of the GC/GC separation. The mixture separated in the GC-GC consists of 5 ketones. The effluent of the first column is pulsed into the second column, so that both separations detected by a single detector.

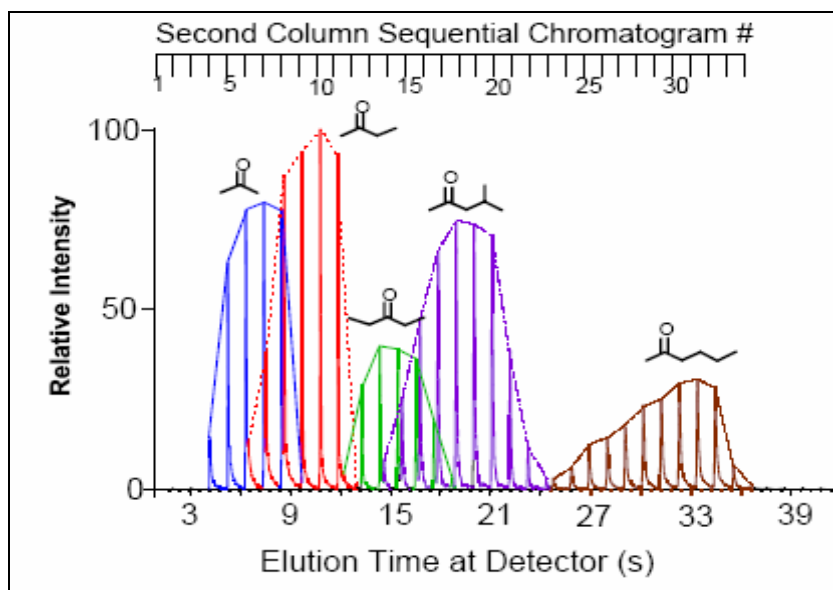


Figure 16. GC/GC separation and detection, using a single detector.

#### 4.2.Reconstructed GC/GC separation

Figure 17, shows the same data as Figure 16, reconstructed into a 2-D contour plot. As it is shown in Figure 16, converting the detector trace to a series of raster lines constructs the 2-D GC/GC separation. The peaks are identified by a number, which is attributed to each compound. These compounds are (1) acetone, (2) methyl ethyl ketone (MEK), (3) diethyl ketone (DEK), (4) methyl isobutyl ketone (MIBK), and (5) 2-hexanone (MBK). The overall outline for each peak (shown by the dotted lines connecting the peak tops) indicates the shape of the low-resolution peaks eluting from the first column.

This contour plot illustrates how the data are rastered with the use of injection into the second column for synchronization. The separation is relatively poor in the first column and provides just a near-baseline separation for the last peak (2-hexanone); the second column provides additional separation to resolve completely the peaks in the two-dimensional map. Moreover, it should be noted that this resolution is largely the product of the 4-s vapor sampling pulses, used for the first injection. These wide pulses ensure that multiple chromatograms may be obtained from the second column for each peak eluting from the first column.

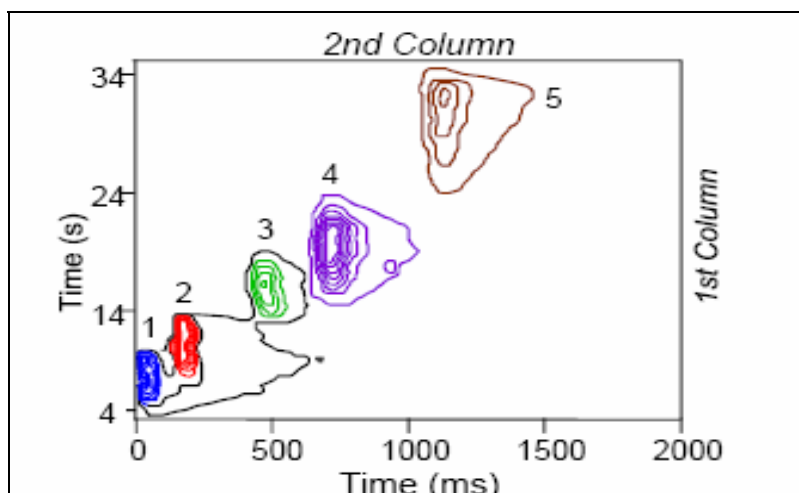


Figure 17. 2-D GC/GC separation (Contour plot).

### 4.3. The future is fast

The key to future field-portable instruments is ultra-fast separations, such as the 1-second chromatogram shown in Figure 18. Ultra fast separation of compounds is needed for quick data processing in the field, in order to have a quick estimation of hazardous environment and address the proper emergency plans.

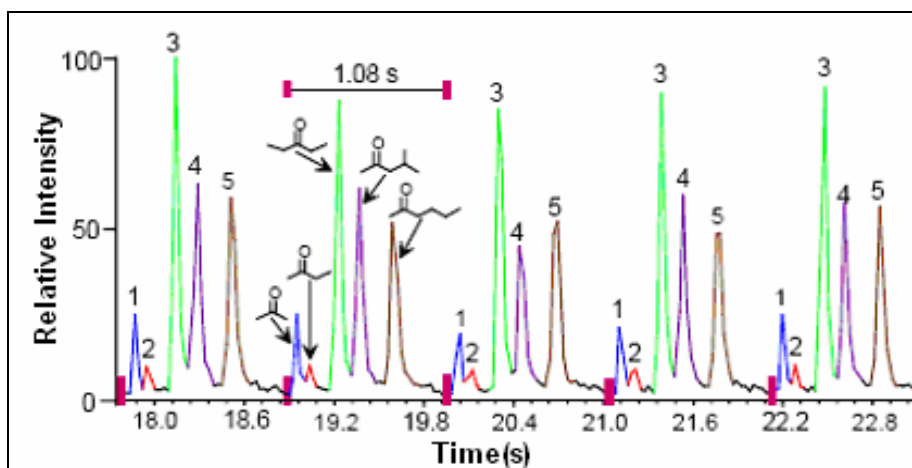


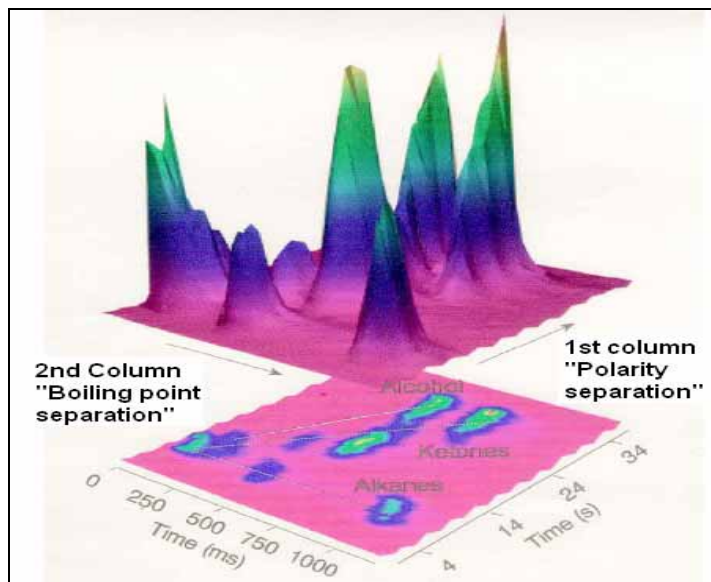
Figure 18. Chromatogram resulted from ultra fast GC-GC analysis.

### 4.4. Second generation GC/GC

Second generation GC/GC provides separations that are performed under the 1 second and can take full advantage of the hyphenated approach. This 2-D separation includes separation of compounds in the first column regarding their polarity and in the second column regarding their boiling point, as shown in Figure 19. The separated compounds are: (1) acetone, (2) methyl ethyl ketone (MEK), (3)



diethyl ketone (DEK), (4) methyl isobutyl ketone (MIBK) and (5) 2-hexanone (MBK), along with three additional compounds, n-heptane, n-octane and 3-methyl 3-pentanol.



*Figure 19. Separation of compounds, depending on their Polarity and Boiling Point, performed in the two columns of a GC/GC instrument.*

Two different properties are being measured in the columns. The first column separations are based on both polarity and volatility, while the second column provides a simple “boiling-point” separation. In this case, it is clear that families of compounds will lie along diagonal lines in the overall data space. In Figure 19, the second separation is obtained in less than 1 s.

#### **4.5.Comparative analysis**

Each of the hyphenated instruments already presented (GC/MS, GC/IMS, GC/GC) have both advantages and disadvantages for field-portable applications. In Table 1, information regarding specifications of field-portable instruments, such as specificity/resolution, sensitivity, speed, size and weight, power consumption, ruggedness and cost of those instruments are given. The grades 2, 3 and 4 were used to indicate good, very good and excellent performance, respectively.



Table 1. Advantages and disadvantages of hyphenated methods.

Hyphenated method	Specificity/Resolution	Sensitivity	Speed	Size & Weight	Power	Ruggedness	Cost
GC/MS	4	3	3-4	2	2	2-3	2
GC/IMS	2	3	3	4	3	3	3
GC/GC	3	2	2	3-4	2-3	3-4	3-4

According to the information given above, it seems that GC/MS and GC/IMS provide very good or excellent sensitivity and speed in the analysis, compared to a GC/GC instrument that is characterized good. However, the GC/GC instrument is very competitive due to its low cost, compared to the other two. This advantage can be achieved though increased automation, reduced sample preparation and reduced original instrument costs, due to lower manufacturing tolerance requirements. This advantage has long been the overlooked motivation for a wide variety of hyphenated instrument applications. It will be proved especially important in applications, such as the detection of highly toxic chemicals in the case of a chemical release, because of the tremendous costs involved in failures to adequately protect workers and the public.

#### 4.6. Distributed systems

Networks of low cost instruments may be deployed to provide real-time mapping of regional effects. In Figure 20, such a map is presented, where a network has been developed through urban-rural interface, longitudinal valley transport, lake, airport, canyon transport, urban forest perimeter and mixing layer.

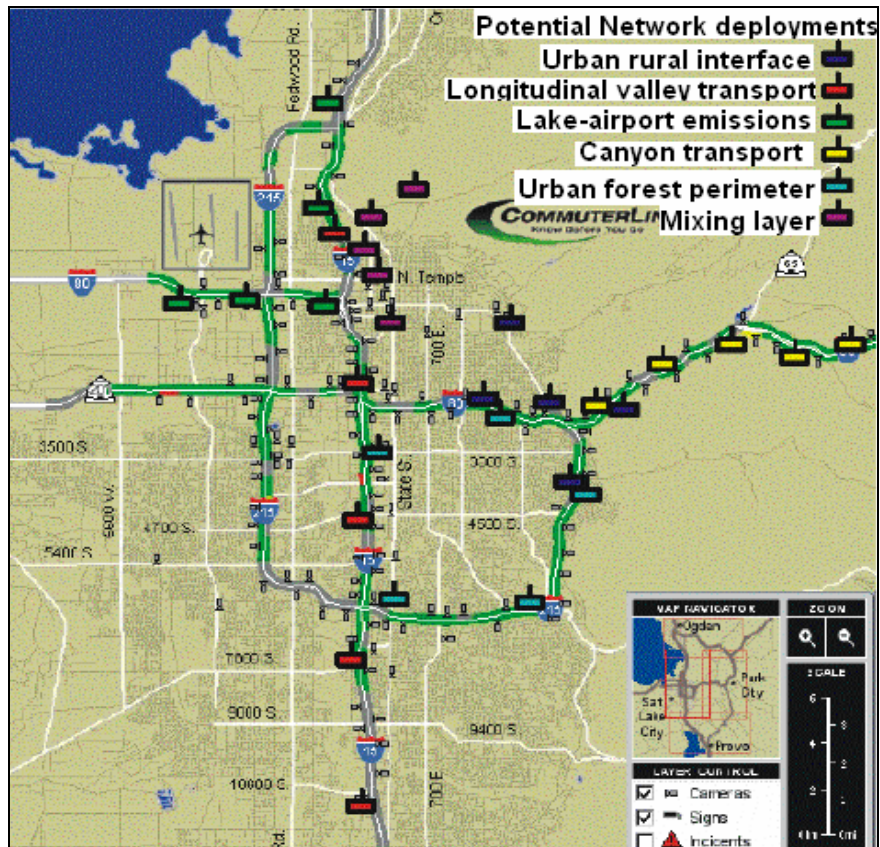


Figure 20. Mapping of regional effects by network of low cost instruments.

## 5. Conclusions

Previous generations of one-dimensional analytical instruments can be large, expensive, non-specific and slow. Hyphenated instruments offer speed, specificity and surprisingly, simplicity. Multiplicative increase of resolution allows fast, low cost, and low-resolution elements to yield extraordinary performance. Moreover, hyphenation offers profound benefits for automation and unattended operation, by eliminating manual sample preparation steps. Low costs will lead to higher spatial resolution experiments, by large-scale instrument deployment.

## 6. Acknowledgements

Kyrptic Technologies, North Salt Lake City, Utah

➤ Ion mobility spectrometry for air-quality monitoring and personal protection  
(W. Vautz, Institute for Analytical Sciences, De)

## 1. Introduction

### 1.1. About ISAS – Institute for Analytical Sciences

ISAS was founded in the 50ies and although at first research directions were towards coal and steel industry they have changed and focused on biochemistry.



Figure 1. ISAS-Institute for Analytical Science.

Other research areas include identification and quantification of all compounds of a complex mixture, known as „...omics“. As a function of time, it is called monitoring, whereas as a function of space imaging (Figure 2).

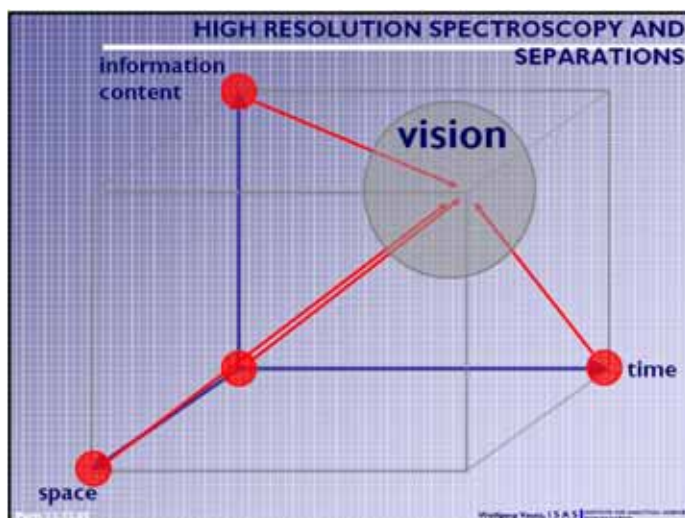


Figure 2. High resolution spectroscopy in space and time.

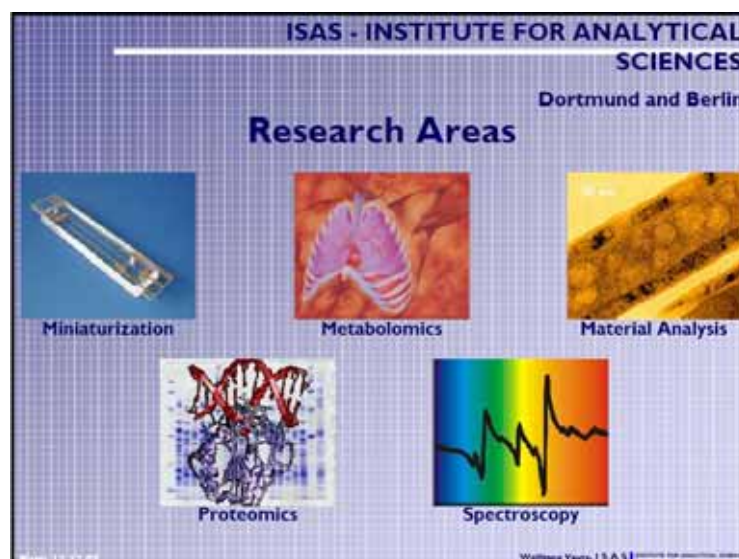


Figure 3. ISAS - Research areas.

Some of those research areas are presented in the following:

### 1.1.1. Miniaturization

When a small sample volume is used, the sample requirement, as well as, the time of analysis can be extremely reduced. Complex analysing systems can be integrated on a surface of a few cm<sup>2</sup>. Sample injection, separation and detection can be automatized and analysing series can be realised with low sample consumption.



Figure 4. Miniaturization of plasmas and analytical instruments.

All projects include the methodic development of total analysing systems, as well as, the performance of chosen applications in order to fulfil the realisation of the method.

### 1.1.2. Metabolomics

Metabolites represent the final products of genetic expression. Qualitative and quantitative analyses provide a view inside the biochemical status or phenotype of a cell or an organism. Such correlations of biochemical information with molecular data will allow much better insight into the function of unknown gene, cell systems or organisms, especially with respect to the response to external stimuli.

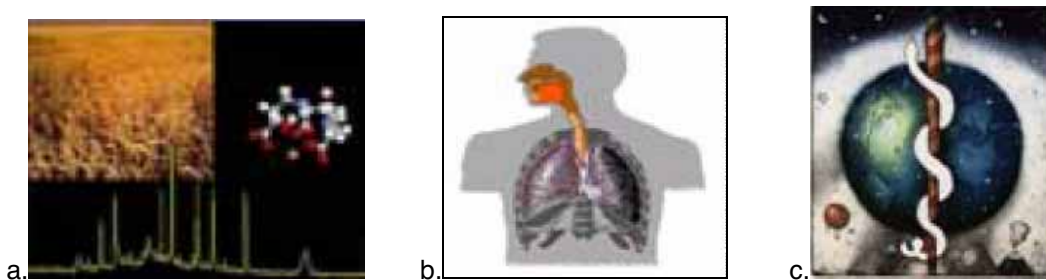


Figure 5. a. Functional diversity of low-molecular-weight metal species in plants, b. Recognition of possible lung cancer using Ion Mobility Spectrometry, c. Pharmaceutical effective plant-extracts.

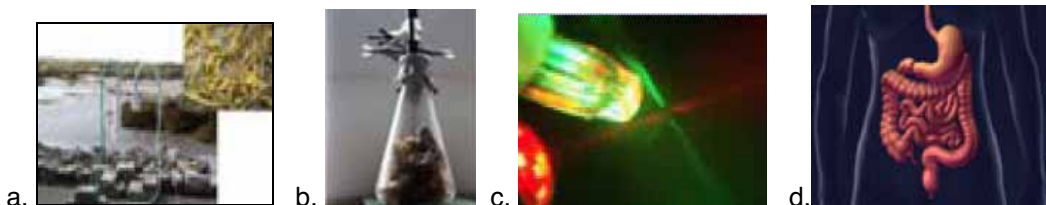


Figure 6. a. Development of mass spectrometric methods for the analysis of organic species from biogenic sources, b. Detection of emissions from mold using Ion Mobility Spectrometry, c. Single particle analysis by LD/APCI/MS, d. Metabolites in human bowel tissue.

Metabolomic studies also offer opportunities to study regulation processes and signaling between cells and inside organisms, under the control of small molecules. Qualitative and quantitative differences in transcriptome, proteome and metabolome level become clearly visible.



## 2. Ion mobility spectrometry

In Figure 7, the basic parts of an Ion Mobility Spectrometer (IMS), (ion source, shutter, drift region and detector), are shown together with the data obtained from the analysis, plotted versus the drift time in msec. Generally, IMS can be combined with chromatographic pre-separation. In Figure 8, the pre-separation of the sample is achieved by using a GC-column or a Multi Capillary Column (MCC), before entering a UV-IMS (Ultra Violet spectroscopy - Ion Mobility Spectrometry) instrument. The ion source of an IMS can be a UV-light, a Partial Discharge (PD) or a  $\beta$ -radiation source, such as  $^{63}\text{Ni}$ . In Table 1, advantages and disadvantages of possible IMS sources are shown. It seems that  $^{63}\text{Ni}$  has many advantages regarding stability and power supply, but it is radioactive. In Figure 9, a contour plot of the analysis data obtained from a GC or MCC column combined with an IMS are shown, where x- axis is attributed to retention time in arbitrary units of the mass spectrometer (a.u.), the y- axis to the drift time in msec and the z-axis to the IMS signal in V.

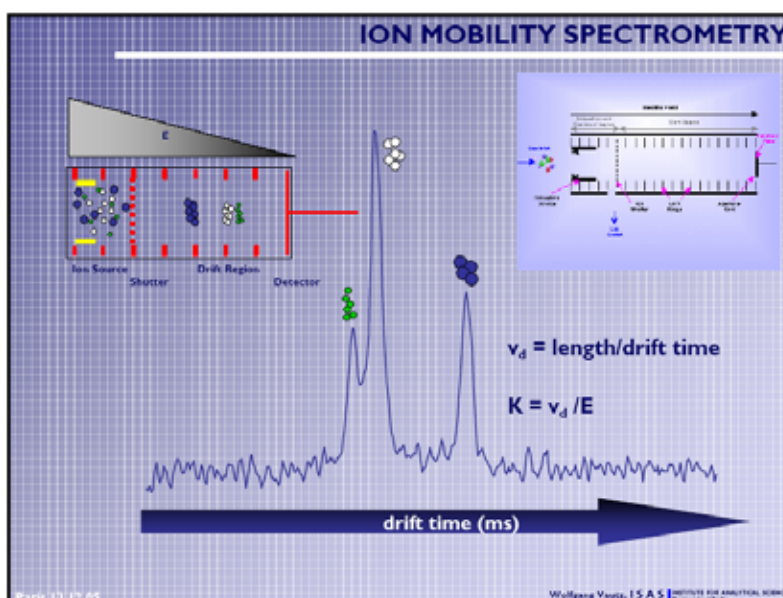


Figure 7. Ion mobility spectrometer and analysis data, plotted versus the drift time.

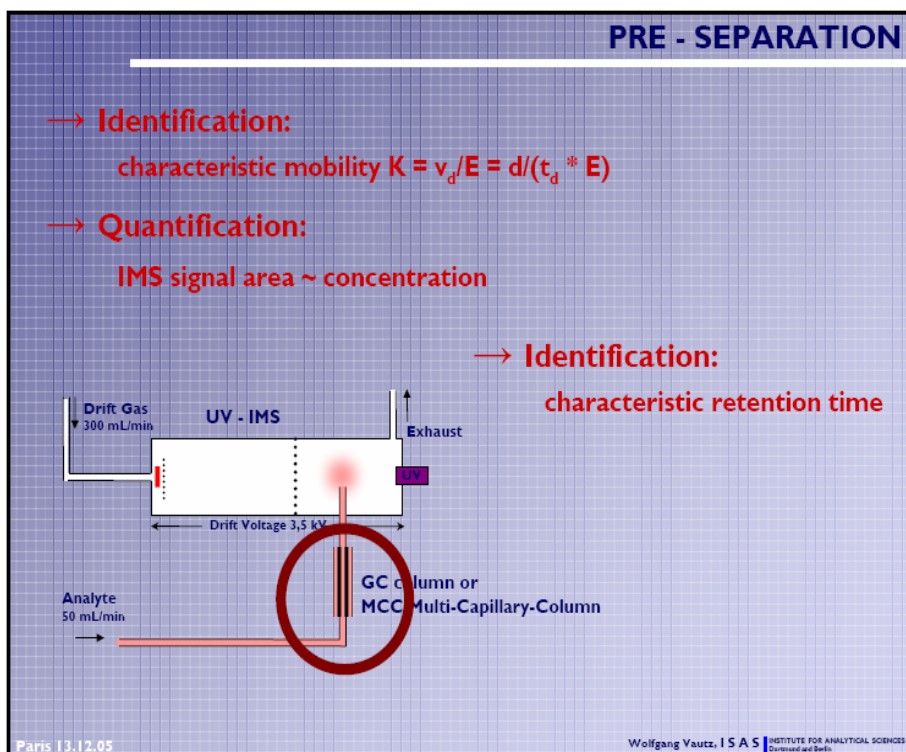



Figure 8. UV-IMS combined with chromatographic separation.

Table 1. Advantages and disadvantages of ion sources.

SOURCE	ADVANTAGES	DISADVANTAGES
UV-light (10.6 eV)	- high stability	- additional power supply - only positive ions
Partial Discharge (PD)	- positive & negative ions	- additional power supply - abrasion of discharge needle
$\beta$ -radiation (63 Ni)	- very high stability - no power supply - positive & negative ions	

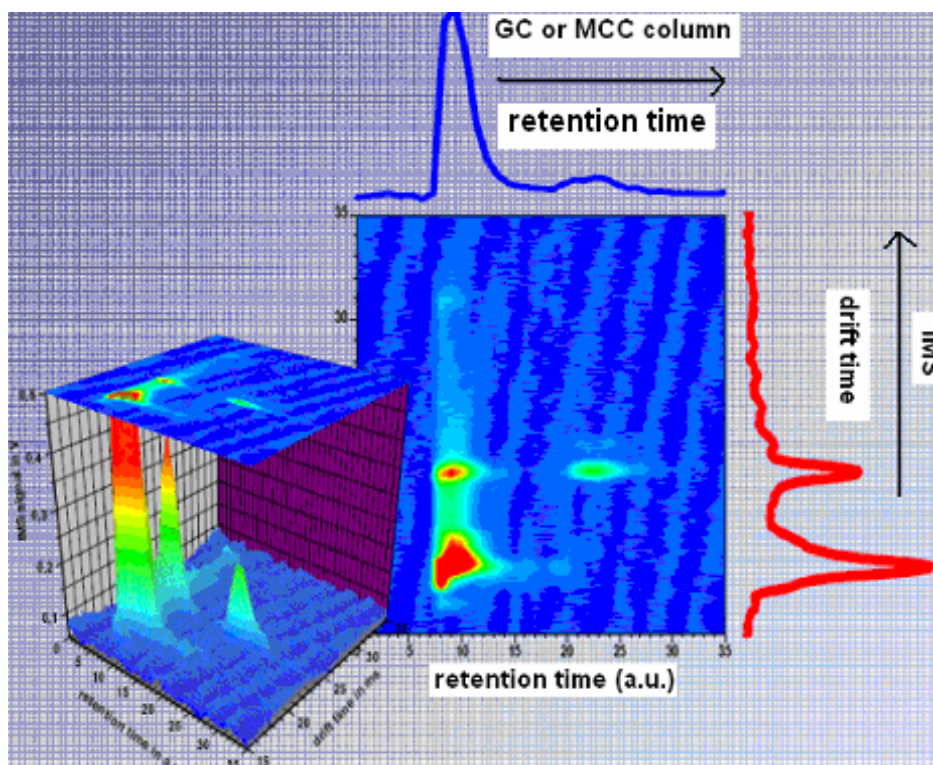


Figure 9. GC or MCC /IMS analysis data, presented as contour plot.

### 3.Excursion: statistics

In Figure 10, original data sets of a  $^{63}\text{Ni}$  IMS with pre-separation are shown, where data are presented as contour plot (x- axis drift time and y-axis retention time).

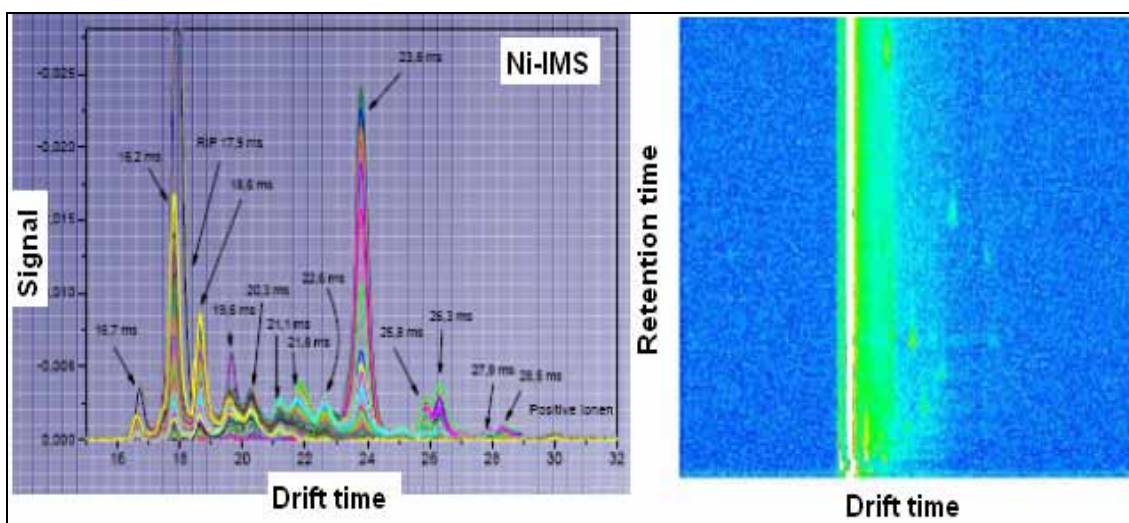


Figure 10. Data sets of a  $^{63}\text{Ni}$  IMS with pre-separation.



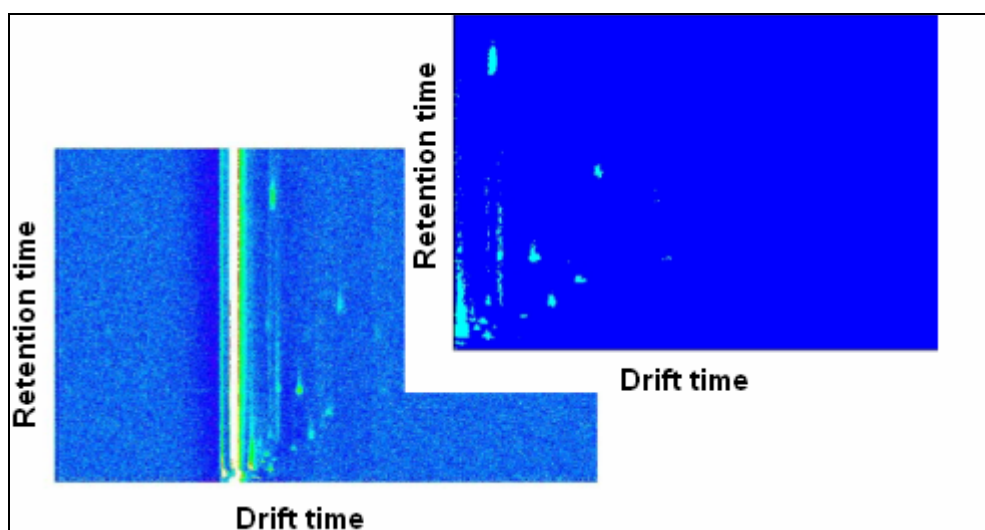


Figure 11. Transformation and class formation in IMS analysis with pre-separation.

Transformation in IMS analysis, combined with pre-separation, includes baseline correction, reduced ion mobility and adjustment of retention time to temperature of MCC. Class formation includes peak-finding, based on a combination of a partition cluster analysis and a bounding-box-algorithm, as well as, a definition of centroids for each detected region (Figure 11).

In order to achieve correct distinction between two samples A & B (Figure 12), the procedure is:

1) *Selection of Variables*

- Use of t-Test.
- Determination of multiple significance (the level is determined by using the Bonferroni-Holm-method).

2) *Discrimination*

- Fisher's Linear Discriminant Analysis.
- Leave-one-out-method, or splitting sample into learn and test sample.

The result of such a procedure is a simplified class formation, a leave-one-out error rate estimation of 0.013 and also a re-sampling estimation.

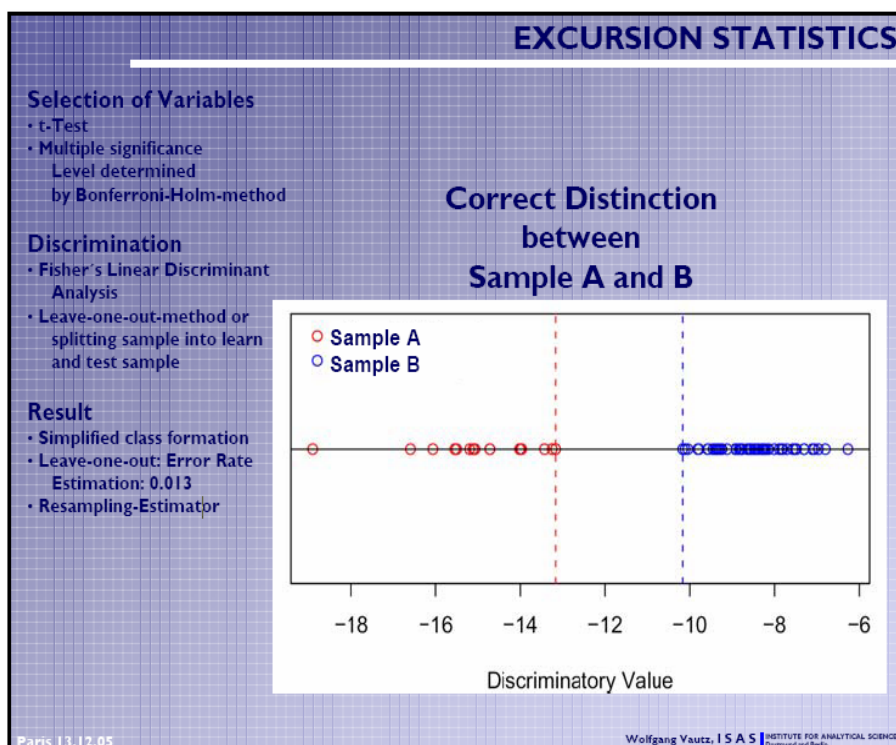


Figure 12. Correct distinction between samples A and B.

#### 4.Applications of IMS

IMS size has been extremely reduced with time, since it was initiated as a laboratory IMS in early 70s. It was become portable in 90s as field-IMS and today its size has been minimized, the so-called miniaturized IMS ( $\mu$ -IMS).

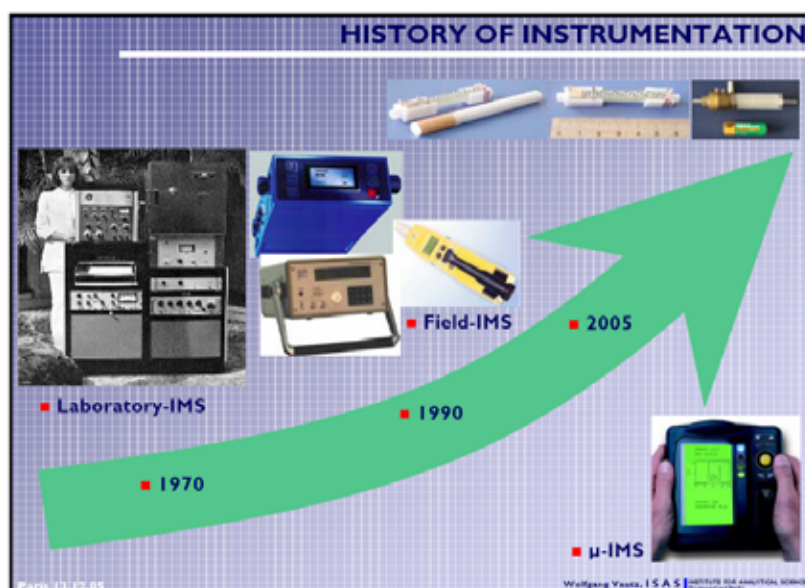


Figure 13. History of IMS from 1970 to 2005.

Some of the non-civilian applications of IMS instruments (Figure14) are for nerve and blister agent detection, as well as, for security in airports (detection of drugs and explosives). More specifically, over a 10.000 IMS analyzers have been distributed to airports and almost 10.000.000 measurements per year take place.

IMS instruments can also have various applications on health sector. More specifically, ISAS has used IMS for the diagnosis of lung diseases. In Figure 15, four contour plots are shown. The first one is attributed to a healthy person (reference). The other three plots (second, third and fourth) are attributed to three different subjects, who according to specific marker compounds that resulted from the IMS analysis of their expired air, they are patients of 1) bronchiectasis, 2) pneumonia infection and bronchiectasis and 3) pseudomonas infection and airway inflammation, respectively.



Figure 14. Non-civilian applications of IMS instruments.

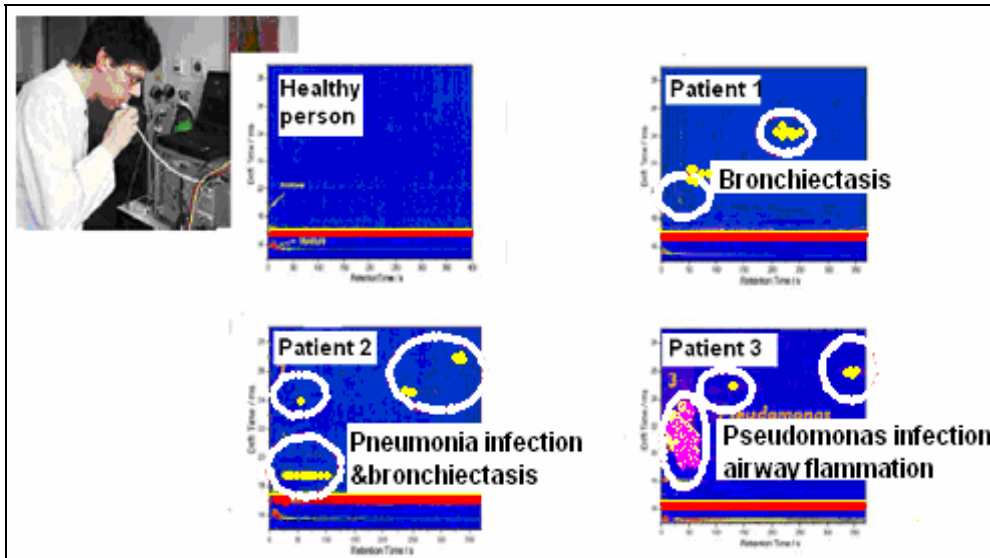


Figure 15. ISAS application of IMS for diagnosis of lung diseases.

In Figure 16, the results from the analysis of expired air by MCC-<sup>63</sup>Ni-IMS have been used for the diagnosis of cancer (compounds in the circles). Moreover, IMS has been used for food quality and safety control, as well as, for packaging characterization (Figure 17).

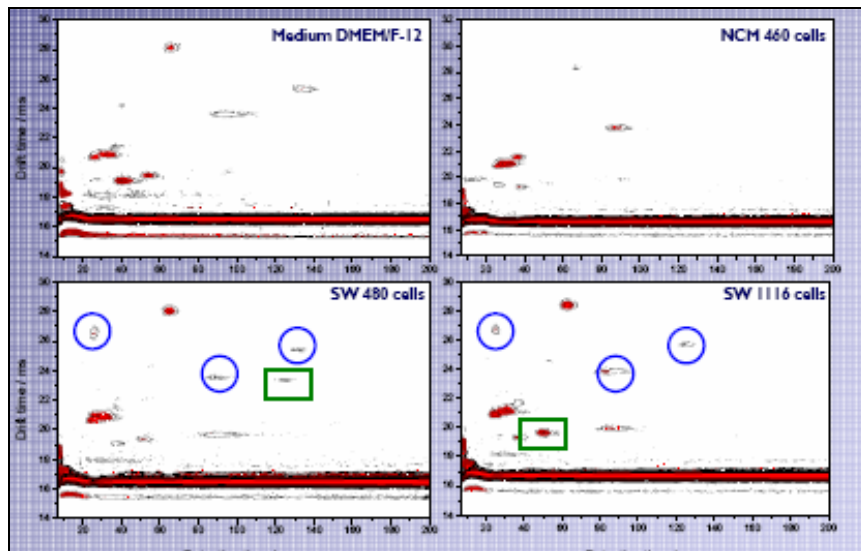


Figure 16. Diagnosis of cancer by MCC-IMS analysis of expired air (ISAS).

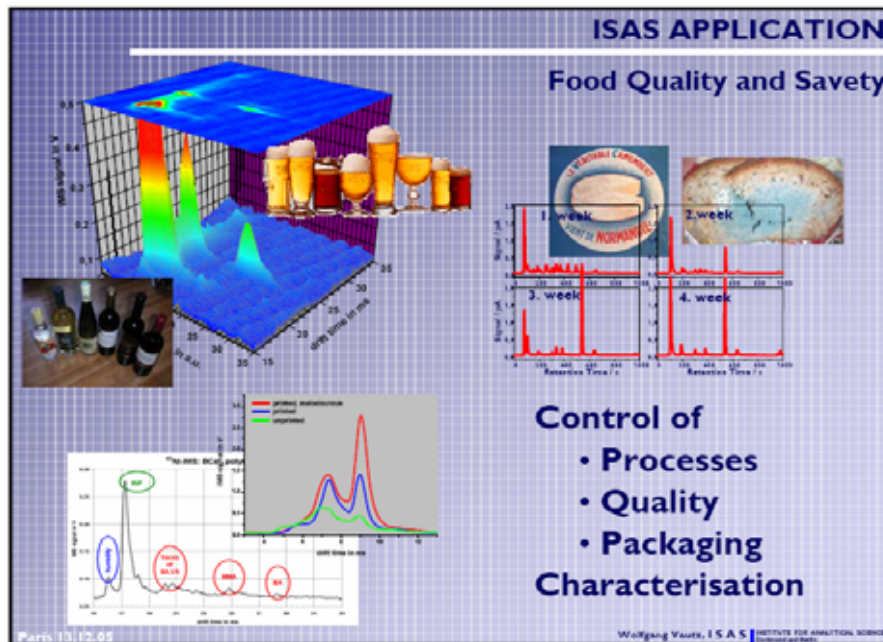


Figure 17. IMS applied on food quality and safety control.

### 5. Air-quality monitoring and personal protection

IMS can be used as personal protective equipment, as long as, it is fast, high sensitive and selective, it has high potential for miniaturization and it is reliable, as long as it is calibrated with an internal standard (Figure 18).

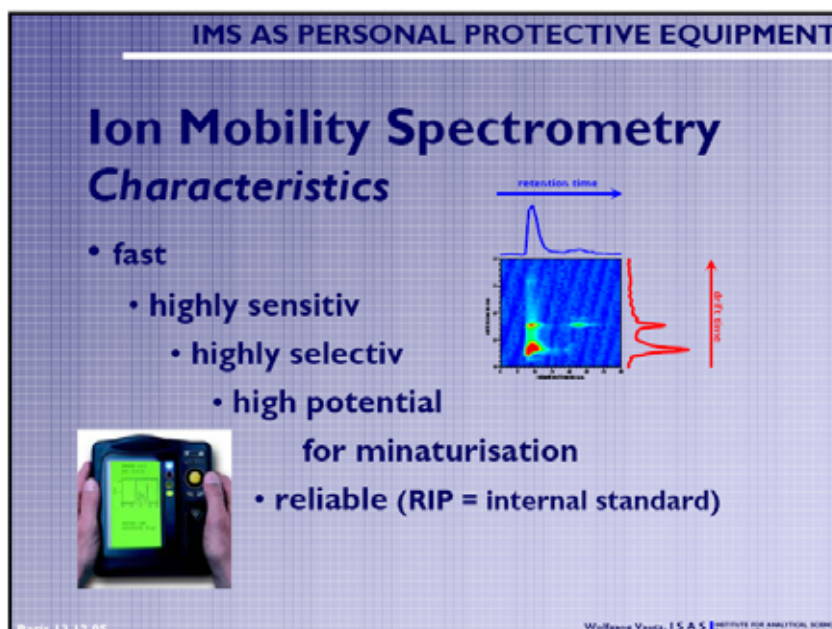


Figure 18. IMS characteristics as a personal protective equipment.

Until now, the traditional method for analyzing a complex mixture of pollutant cloud was the use of simultaneous test passive tubes (Drager).



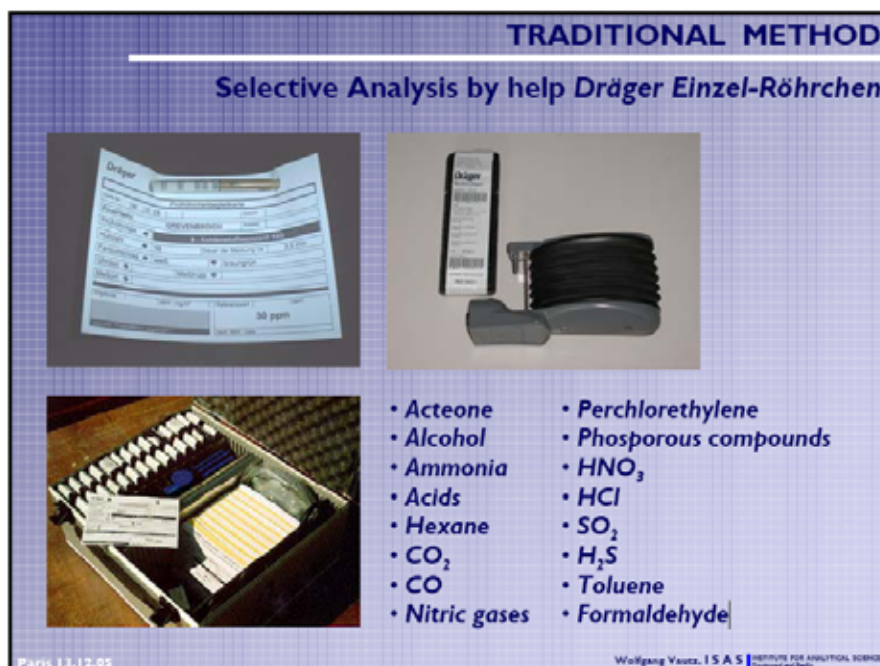


Figure 19. Selective compounds analyzed by Dräger tubes.

In Figure 19, a group of selective compounds that can be analyzed by dräger tubes are shown. Instead of using multiple sorbent tubes for simultaneous analysis of different pollutants, IMS can be used for the on-line analysis of different compounds. In Figure 20, organic and inorganic groups that can be simultaneously analyzed by using a  $\mu$ -IMS ( $^{63}\text{Ni}$ -IMS and 10,6 eV UV-IMS) are shown (e.g. ketones, aromatics, alcohols, aliphatic and chlorinated hydrocarbons). According to G.A. Eiceman and Z. Karpas, (Ion Mobility Spectrometry, CRC Press, Boca Raton, 2005) ion mobility spectras and reduced ion mobilities are available for more than 220 analytes.

Portable devices, which can provide on-line monitoring of air-quality quickly and reliably, such as  $\mu$ -IMS, can be useful tools for the personal protection, especially of the operational people that have to move very quickly in the field (e.g. in the case of a chemical accident). The new approach is the use of  $\mu$ -IMS integrated to clothes, so that the resulted uniform (Figure 21) to be not only an effective personal protective equipment but a sensor as well; in that way, personnel (e.g. the fire-fighters) can be informed for their exposure near the flame-front and decide on evacuation of place on time.

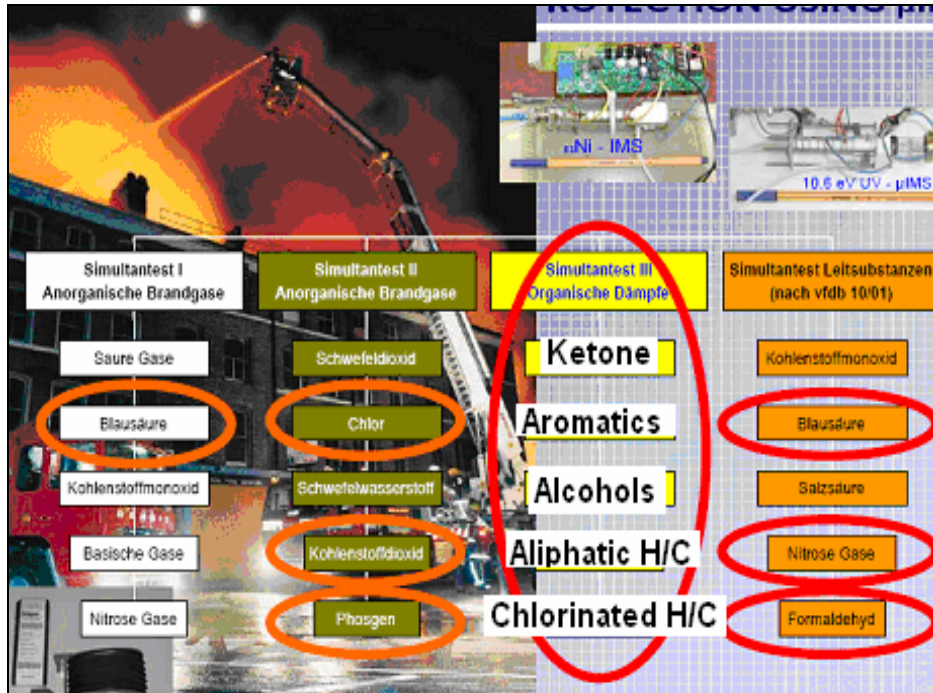


Figure 20. Group of compounds that can be analyzed by  $\mu$ -IMS.

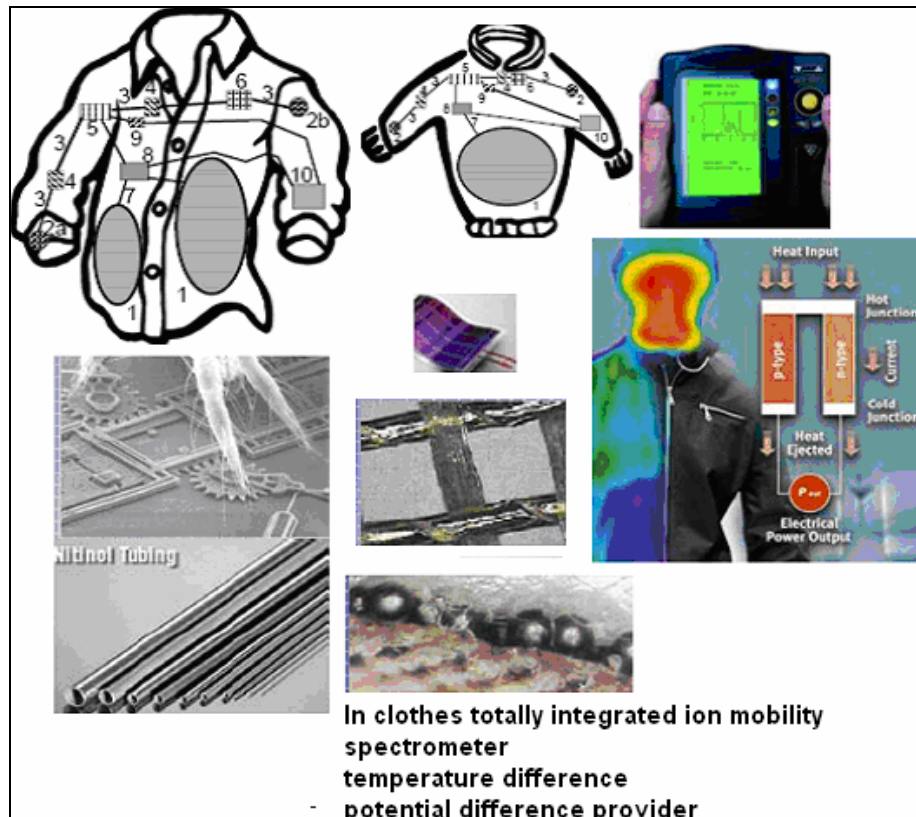


Figure 21. IMS integrated to a uniform as a mean of protection.

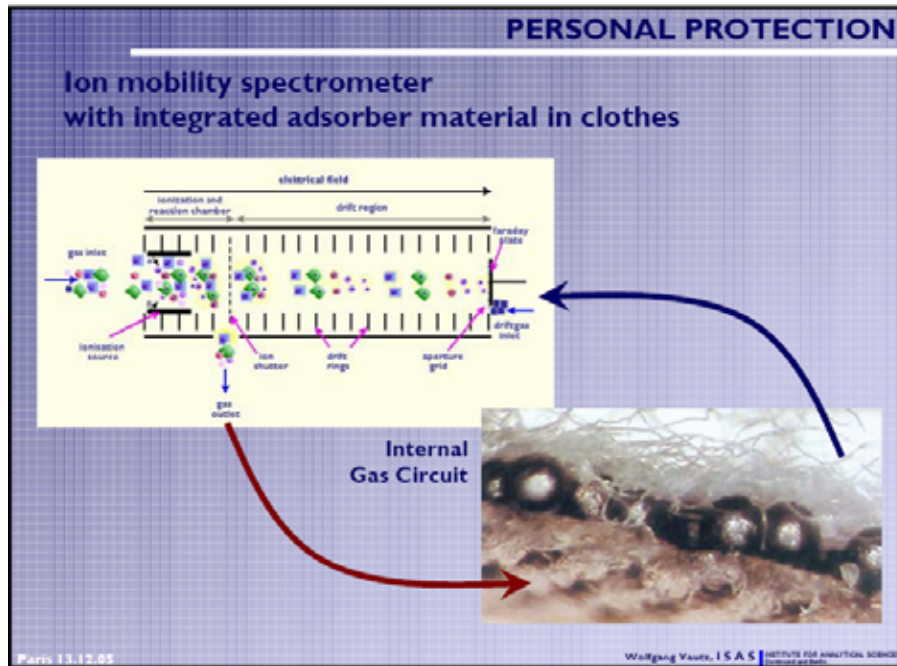


Figure 22. IMS totally integrated to clothes.

In Figure 22, the way that an IMS is totally integrated to clothes (e.g. uniform of personnel) is shown. The gases are absorbed by the material cloth and analyzed by the  $\mu$ -IMS through an internal gas circuit. Evaluation of data takes place by the Gaspector software (Figure 23).

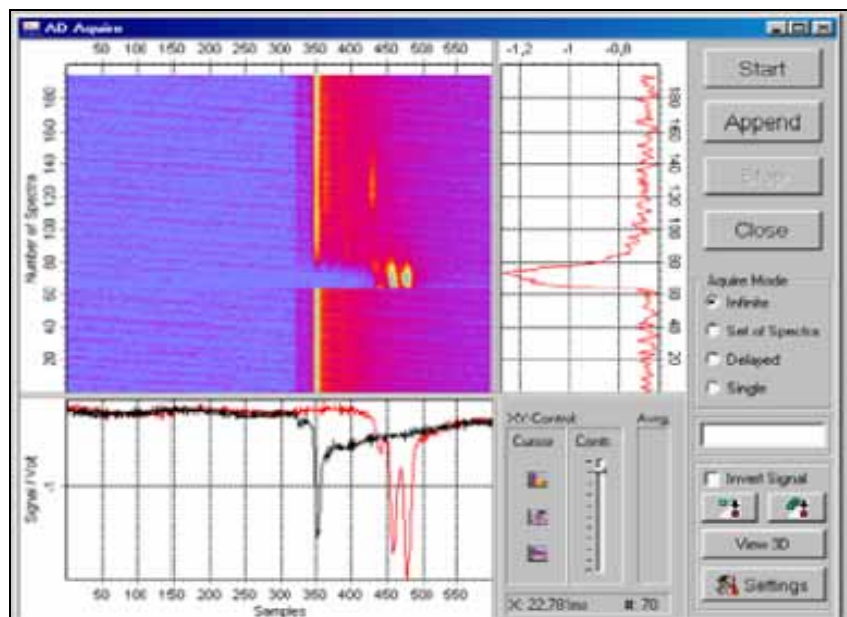


Figure 23. Data evaluation by using Gaspector software.



## 6. Conclusions and outlook

### 6.1. Air-quality monitoring in a forest fire through a $\mu$ -IMS network

According to the above, IMS technology can be used for the on-line analysis of the complex mixture of forest fire smoke, as long as, in a forest fire incident fast and reliable analysis is needed, in order to decide on emergency response actions and protect fire-fighters and the exposed population.

The idea, as it is shown in Figure 24, is in the fire incident: 1) each group of the fire fighters to have a portable  $\mu$ -IMS with them, either as a device, or as an integrated instrument to uniforms and/or 2)  $\mu$ -IMS instruments to be put in specific sites of the perimeter of the forest fire. The analysis data of all the instruments will be transferred to a mobile/airborne data central unit, where data acquisition, calibration and evaluation will take place. In sequence, after determining concentrations of the smoke pollutants in the specific sites, warning signals for possible evacuation of the area and directions will be sent to the firemen crews, taking also into consideration meteorological data, such as wind speed and direction. All necessary information will also be sent to services, such as police, fire department and civil protection.

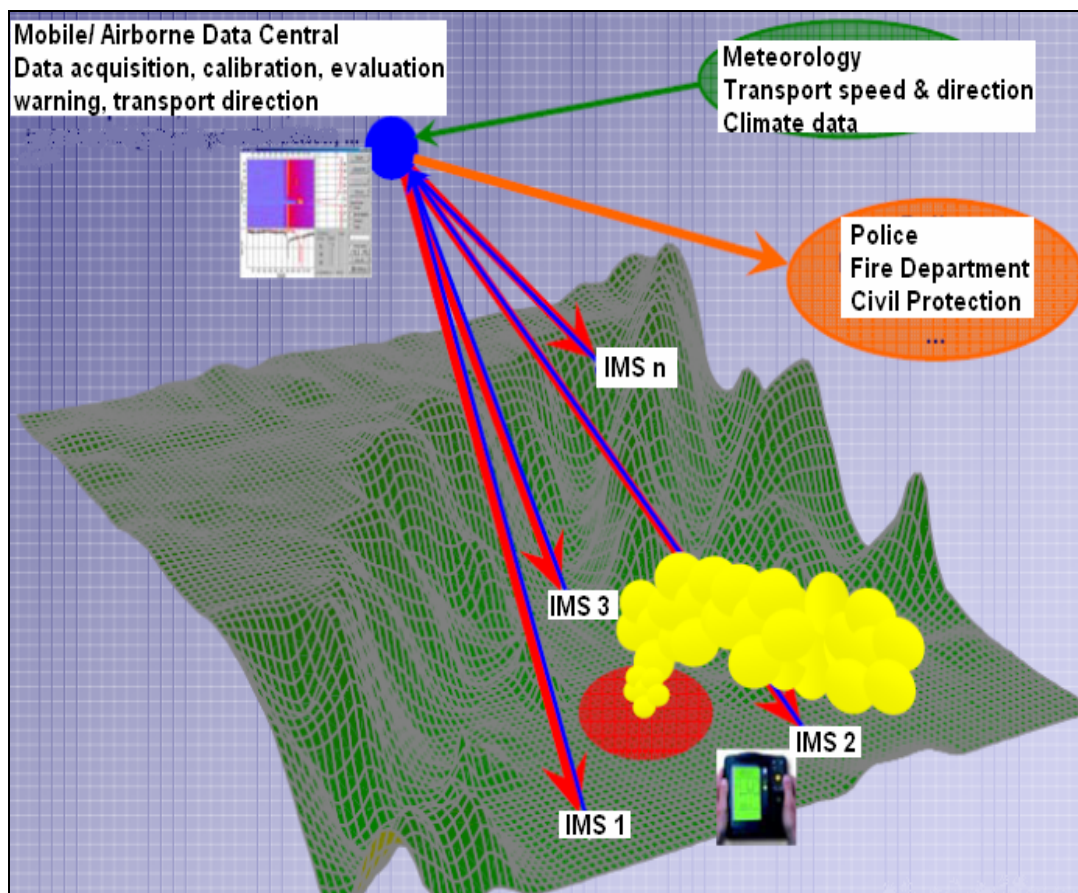


Figure 24. Using a  $\mu$ -IMS network for air-quality monitoring in a forest fire.

Such a network will be very effective for the protection of the firemen crews. Although it might be seem complicated it can be achieved, as soon as, components are available and the only thing required is effective combination of existing technology and means.

➤ **Monitoring of air pollution over an urban site using a mobile backscatter LIDAR (Light Detection And Ranging technique) system**  
(*G. Chourdakis, G. Georgousis, K. Hondidiadis and A. Ikonou, Raymetrics S.A., Gr*)

### **1.Introduction**

Laser remote-sensing techniques (LIDAR systems), have gained high acceptance as long-range non-invasive probes of the chemical composition and the physical properties of the atmosphere. The detection and analysis of the received LIDAR signals permit the retrieval of the relative concentration of the suspended aerosol particles and of the absolute concentration of several air pollutants (i.e. O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub> etc.), with high temporal and spatial resolution (1 min and 3,75 m respectively) along the propagating laser beam (M. Dell Aglio et al, Optics and Lasers in Engineering, 37 (2002) 233). For the measurements of gases and suspended aerosols, laser light extinction, as well as, elastic and inelastic (Raman) scattering are used (D. Whiteman, Applied Optics, 42 (2003) 2571).

Therefore, the LIDAR technique has become a very powerful tool to visualize, in real-time: a) the atmospheric dynamical transport processes, using the aerosol particles as tracers, b) the vertical distribution of aerosol particles, either produced locally over the measuring site (car traffic, domestic heating, industrial activities etc.), or transported by the atmospheric circulation (land-sea breeze circulation, trans-boundary air pollution, desert dust events etc.) and c) the structure of the lower atmosphere (structure of the PBL (Planetary Boundary Layer), identification of several aerosol dust layers) and its correlation with ground air pollution levels (G. Vaughan, Encyclopedia of Atmospheric Sciences, Academic press, 2002).

## 2. Methodology

### 2.1. The LIDAR technique

When a laser beam is sent into the atmosphere, it is widely scattered by the suspended aerosol particles, molecules and atoms present in the air. In a typical LIDAR, the backscattered light is collected by a telescope in a coaxial or biaxial configuration, in respect to the laser emitter (Figure 1). The signal is then focused onto a photo-detector through a spectral filter, adapted to the laser wavelength. Since a pulsed laser is used, the intensity of the backscattered light can be recorded as a function of time and thus provide the required spatial resolution of the measurement (D. Althausen et al., Journal of Atmos. Oceanic Technol., 17 (2000) 1469).

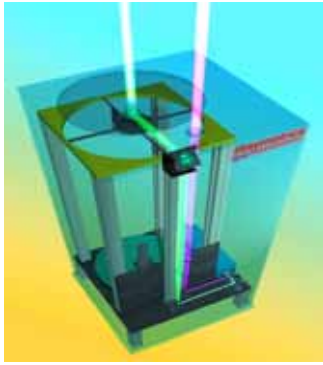
The basic LIDAR equation is given by:

$$P(z) = P_0 \frac{c\tau}{2} \beta(z) A_{tel} O(z) \frac{1}{z^2} \exp \left[ -2 \int_0^z a(z^*) dz^* \right] \quad (1),$$

where,  $P(z)$  is the detected backscattered radiation from range,  $z$ ,  $P_0$  is the laser output power,  $\tau$  is the laser pulse duration,  $c$  is the speed of light,  $\beta(z)$  is the volume backscatter coefficient,  $a(z)$  is the total atmospheric extinction coefficient,  $A_{tel}$  is the total telescope area and  $O(z)$  is the overlap function, which takes into account geometrical and optical factors of the receiver arrangement (G. Chourdakis, A. Papayannis and J. Porteneuve, Applied Optics, 41 (2002) 2715). The extinction term  $a(z)$  includes the contribution of the different absorbing atmospheric molecules ( $O_3$ ,  $NO_x$ ,  $SO_2$ , etc.) and aerosol particles.

### 2.2. LIDAR system hardware

The Raymetrics LB11 LIDAR system is designed and manufactured by Raymetrics S.A., in order to perform continuous measurements of suspended aerosol particles in the Planetary Boundary Layer (PBL) and the lower free troposphere (Figure 2). It is based on the second harmonic frequency of a compact pulsed Nd: YAG laser, which emits pulses of 65 mJ with output energy at 532 nm, with a 10 Hz repetition rate. The optical receiver is a Cassegrainian reflecting telescope with a primary mirror of 200 mm diameter, directly coupled to the LIDAR signal detection box. Inside the detection box, a polarization cube splits the incoming radiation into its two orthogonal polarization components. The two detectors are operated in the photon-counting mode and the corresponding spatial raw resolution of the detected signals is 3,75 m.



*Figure 1. Typical configuration of the Raymetrics LB20 dual-beam LIDAR system with one coaxial and one biaxial laser beam, with respect to the optical axis of the receiving telescope.*



*Figure 2. The Raymetrics LB11 LIDAR system designed and developed to perform continuous measurements of the suspended aerosols particles in the PBL and the lower free troposphere.*

### **2.3. LIDAR system analysis software**

The LIDAR is equipped with dedicated software for setting-up and operating the system, as well as, several software modules for automatic data acquisition, data analysis and visualization. Raw data are stored in a database, providing data mining capabilities and extensive compatibility with other commercial programs. The Klett inversion technique is used to retrieve the vertical profile of the aerosol backscatter coefficient at the respective wavelengths (J.D. Klett, Appl. Optics, 20 (1981) 2). The final output data include:

- i) Aerosol optical parameters, such as the backscatter coefficient, the extinction coefficient and the depolarization ratio of the suspended aerosol.
- ii) Meteorological parameters, such as the optical depth, the cloud height and thickness, the height and the temporal evolution of the PBL and dust layers.
- iii) LIDAR related parameters, such as the LIDAR Range Corrected Signal (RCS), the Logarithm of the RCS (LRCS) and the first and second derivatives of the RCS and the LRCS.

### 3. Results and discussion

#### 3.1. Tropospheric aerosols monitoring

Tropospheric aerosols arise from natural sources, such as wind-borne dust, sea spray and volcanoes, as well as, from anthropogenic sources, such as combustion of fossil fuels and biomass burning activities. With the increasing urbanization and industrialization, the content of aerosols particularly in the lower troposphere increases continuously (J.H. Seinfeld and S. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, J. Wiley and Sons Inc., New York, USA, 1998).

A backscattering LIDAR system is able to provide accurate data on the spatial and temporal evolution of the suspended aerosols in the troposphere. In Figure 3a, the vertical distribution of the aerosols backscatter coefficient is presented for one case of high aerosol loading. In Figure 3b, the vertical distribution of several cloud layers is presented.

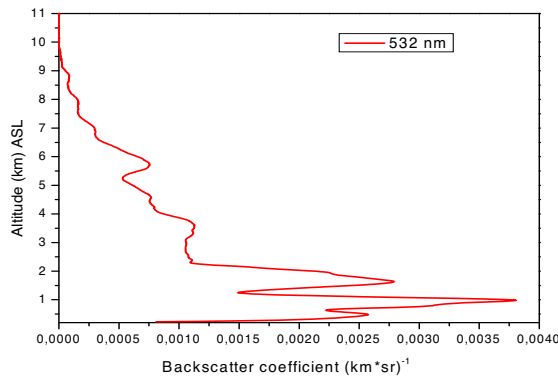


Figure 3a. Vertical distribution of the backscatter coefficient for a typical case of high aerosol loading over the area of Athens, Greece on 20/08/2004 (12:54 UTC).

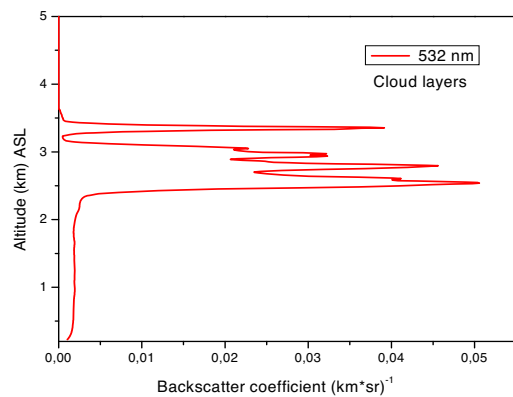


Figure 3b. Vertical distribution of the backscatter coefficient for a typical case of cloud layers over the area of Athens, Greece.

### 3.2.Sahara dust

Large quantities of dust particles are emitted in the atmosphere in desert regions of high convective activity annually. Most of these particles are coarse (diameter  $\geq 1 \mu\text{m}$ ) and hence, are deposited close to their source, while a large fraction of the smaller particles can be transported over very long distances (S. Rodriquez et al., Atmos. Environ., 35 (2001) 2433).

The elastic backscatter LIDAR station in operation in Athens, Greece, by Raymetrics has monitored several extreme aerosol events over the Eastern Mediterranean Sea. The vertical distribution of the backscatter coefficient of the suspended particles in a typical Sahara dust event is shown in Figure 4a. The temporal evolution of the event is shown in Figure 4b.

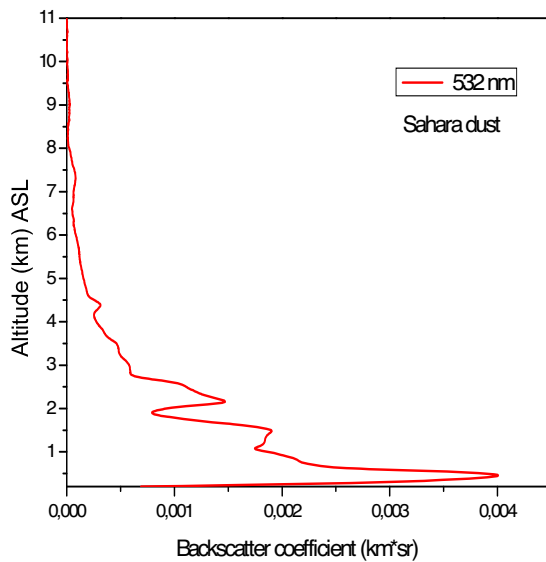


Figure 4a. Vertical distribution of the aerosol backscatter coefficient for a typical case of Sahara dust transportation over the area of Athens, Greece on 18/08/2003 (18:24 UTC).

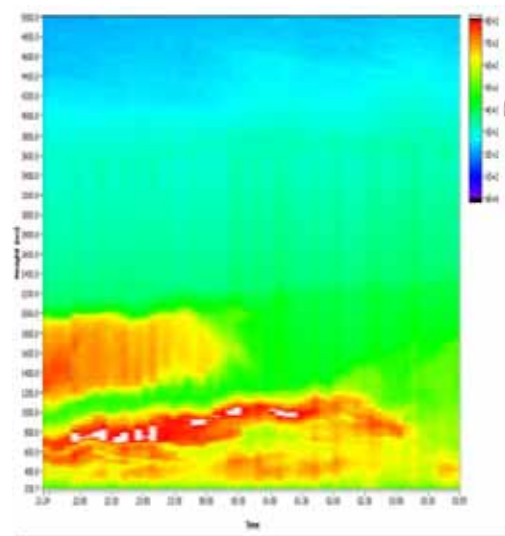


Figure 4b. Temporal evolution of the LIDAR Range Corrected Signal (RCS). The x-axis is UT Time, the y-axis is altitude ASL (m) and the color scale shows the intensity of the LIDAR RCS.

### 3.3. Monitoring of the Planetary Boundary Layer (PBL) height

The Planetary Boundary Layer is the lowest part of the troposphere that is directly influenced by the earth's surface and responds to surface forcing, with a time scale of an hour or less (R. B. Stull, An Introduction to Boundary-Layer Meteorology, Kluwer Academic Publishers, Norwell, MA, 1988). This layer is of primary importance for the entire ecosystem. Air pollutants concentrations in the PBL are generally orders of magnitudes higher than in the free troposphere. Accurate determination of the PBL height is crucial for photochemical and dispersion models, for the accurate prediction of pollutant's concentration. This layer is typically moister and has greater aerosol content than the free troposphere, causing more scattering of laser light.

Therefore, LIDAR can easily detect the boundary between these two layers, with high spatial and temporal resolution. In this study, the PBL height is determined by using the Inflection Point Method (IPM), proposed by Menut et al., (Applied Optics, 38 (1999) 945). This technique is applied on a series of LIDAR data taken over Athens on July 12, 2004 (Figure 5a). The minimum value of the second derivative of the range-corrected signal (RCS) determines the PBL height. In this case it was found at 1083,6 m, which corresponds to the actual PBL height over Athens at 06:00 UTC.

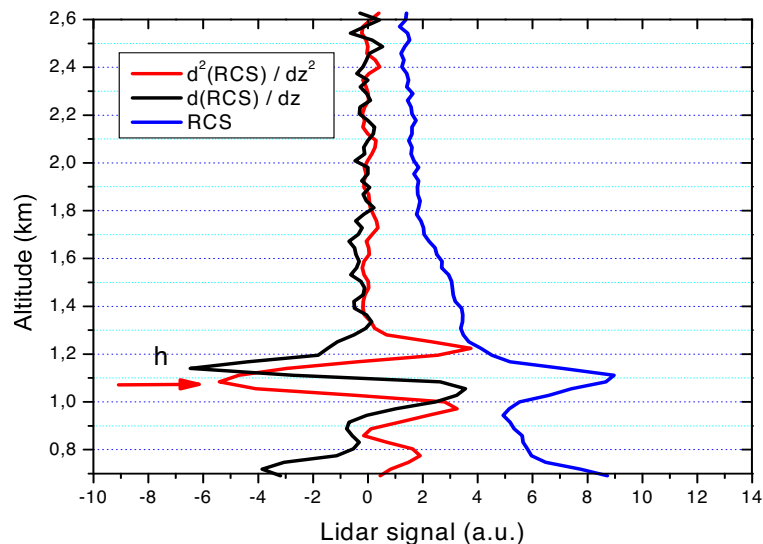
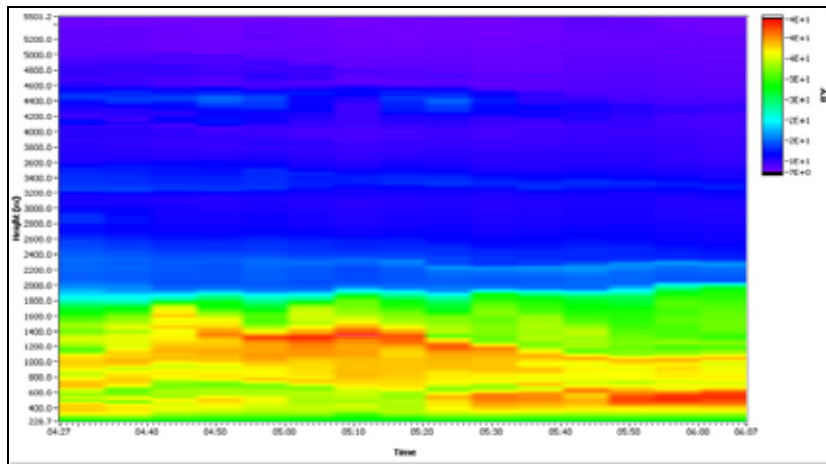


Figure 5a. The vertical profile of the LIDAR RCS (third-line), the first-derivative (first-line) and the second-derivative (second-line) of the RCS are presented. The PBL height on 12/07/2004 at Athens, Greece is determined to be 1083,6 m.



*Figure 5b. Temporal evolution of the LIDAR Range Corrected Signal (RCS) over Athens, Greece on 12/07/2004. The x-axis represents the UTC time, the y-axis represents altitude ASL (m) and the color scale shows the intensity of the RCS. The PBL height can be accurately determined by applying the IPM method on those time plots.*

#### **4. Conclusions**

The present study demonstrates that a compact, small-size LIDAR system can be used to monitor the characteristics of the lower troposphere with great accuracy and reliability. Predicting pollution events in urban areas, such as Athens, requires a good knowledge of the dynamic processes that take place in the lower troposphere. Laser remote sensing is a useful tool for probing the composition and physical state of the atmosphere and for performing measurements at locations that cannot be monitored by conventional detection methods.

LIDAR offers the only realistic measurement technique that is able to retrieve the basic meteorological and atmospheric parameters, as well as, the concentration of the suspended aerosol particles, in real-time. In this study, some of the prospects of the LIDAR technique have been demonstrated. LIDAR technology has matured over the last decade and the future of laser remote sensing appears to be very promising. This statement is supported by many factors that include: (i) the development of practical, compact, eye-safe LIDAR systems, (ii) further reduction of LIDAR system complexity, cost and size and (iii) the use of LIDAR systems in air pollution measurement networks.



## **5.Acknowledgments**

Part of this work was supported by the HIRON Research Project of the Greek General Secretariat for Research and Technology of the Ministry of Development, under contract HR-25.

### **➤Application of LIDAR on forest fire smoke monitoring**

***(G. Chourdakis, Raymetrics S.A., Gr, M. Statheropoulos, European Center for Forest Fires, S. Karma and G. Koutoula, National Technical University of Athens, Gr)***

#### **1.Introduction**

Forest fires produce significant quantities of smoke, affecting directly the exposed receptors, such as the population and the infrastructures. Thus, techniques that can provide information regarding early detection of a forest fire and prediction of the smoke plume pathway are critical to control possible adverse impacts of ffs. LIDAR technique, which has been used so far for air pollution measurements, is such a method that may be applied on forest fire smoke measurements.

#### **2.Forest fire detection using LIDAR**

Forest fires are considered to be a physical catastrophe with devastating social and economic impacts. In order to reduce the burned area, early detection of forest fires and therefore, immediate suppression by the fire-fighting means is critical.

Currently, detection of forest fires is carried out by observers or by means of passive sensing systems, such as near-infrared cameras. Aerial means have also been used for forest surveillance. However, their detection range depends on environmental and weather conditions. More specifically, since they are line-of-sight systems (Figure 1), their detecting capability is mainly reduced in mountainous areas. Alternatively, active sensing methods for fire detection may be based on LIDAR. The advantages of active compared to passive sensing methods, are the longer sensing distances, the constant sensitivity, independence from atmospheric conditions and accurate determination of the distance to the fire. LIDAR has been used for studying the atmosphere and wind regimes, as well as, for military applications and in remote sensing. Though, LIDAR equipment has the limitations of cost, size and easy to use. However, there has been an effort to develop a simple, biaxial monostatic LIDAR for the detection and study of forest fires (A. B. Utkin et al., International Journal of Wildland Fire 12 (2003) 159).

In field tests that took place under the framework of a project (GESTOSA), the researchers have successfully detected experimental campfires, produced by burning dry grass and olive logs at a rate of just 0.02 kg/s up to distances of 6.5 km. Monitoring of smoke particles by using a LIDAR system has also been used for the detection of forest fires (preliminary results), as shown in Figure 2.

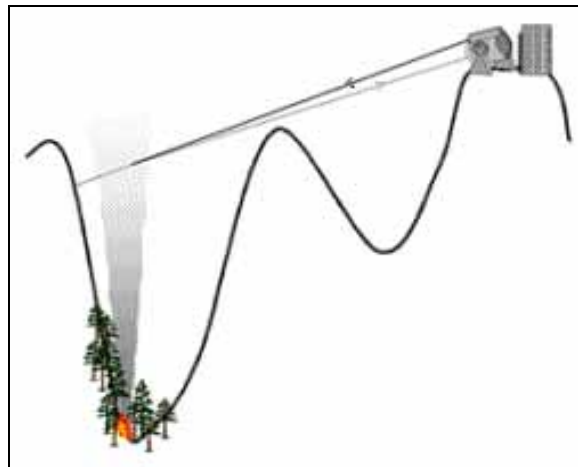


Figure 1. Line-of-sight fire detection system.

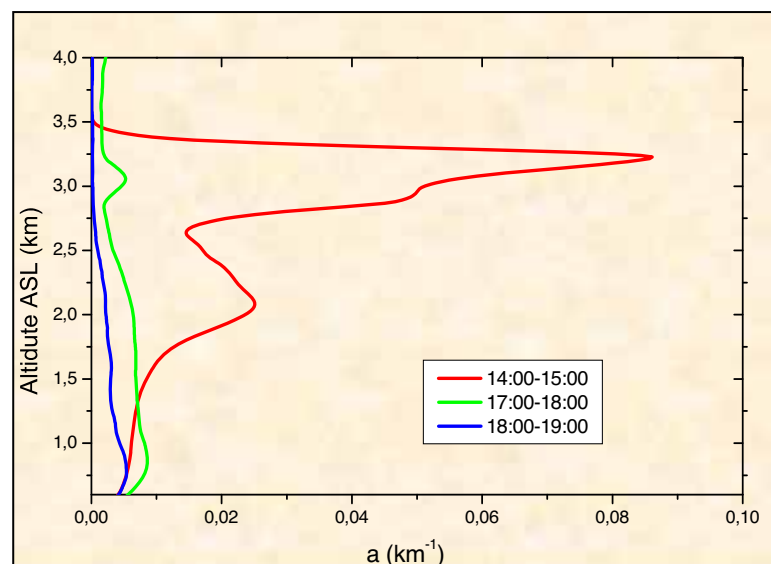


Figure 2. Vertical distribution of smoke particles over the area of Athens in a forest fire (Unpublished data of Raymetrics S.A.).

### **3. Dispersion of forest fire smoke using LIDAR**

Dispersion of forest fire smoke (ffs) has been studied through direct-detection LIDAR measurements and a Reynolds-averaged Navier–Stokes fluid dynamics model (A. Lavrov et al., International Journal of Thermal Sciences, in press). More specifically, LIDAR was used for the 3-D distribution of particle concentrations in ffs plumes, based on data derived from two sources: LIDAR measurements of smoke plumes emanating from experimental forest fires and results of numerical calculations based on the 3-D Reynolds averaged Navier–Stokes equations. The LIDAR measurements provided information regarding the particulate matter distribution, while the numerical model was used for the combustion products: particulate matter (soot), CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>, hydrocarbons and other gases.

Pollutants released from forest fires can travel thousands of kilometers to heavily populated urban areas. Transportation of air pollutants in the free troposphere is more efficient than in the mixed layer, because of fewer loss mechanisms and stronger winds (T. Holloway et al., Environ. Sci. Technol. 37 (2003) 4535). The impact of the July 2002 Canadian forest fires on PM air-quality in Baltimore was assessed using an array of methods (A. Sapkota et al., Environ. Sci. Technol., 39 (2005) 24). The existence of the smoke plume above Baltimore before the peak of the episode and its re-entrainment into the mixed layer during the episode was determined by using a LIDAR.

### **4. Early warning system for forest fire smoke impacts**

Forest fire smoke (ffs) chemical composition near the flame-front is considered critical information for the operational managers, in order to take decisions for the protection of the exposed personnel, i.e. the use of effective personal protective equipment or fast escape from the fire scene.

An integrated operational tool (chemical & laser method), for the on-line field monitoring of the ffs composition near the flame-front, has been proposed as one of the essential characteristics of an early warning system, presented in EWS III conference (2006), organized by UNISDR ([www.fire.uni-freiburg.de/fwf/ews.htm](http://www.fire.uni-freiburg.de/fwf/ews.htm)). The system will carry out measurements, in time and space, in a distance from the flame-front and also near it, by using a combination of LIDAR and a mobile analytical unit. The mobile unit could provide data complementary to that of LIDAR. This integrated system will have specifications adjusted to the heavy and hostile environment of a forest fire and will be used for the on-line monitoring and 3-D mapping of ffs pollutants near the flame-front, qualitatively and semi-quantitatively (profiles, levels).

Data from LIDAR and the mobile unit will be transferred through wireless communication to a data-logging center, where assessment will take place; information will be transferred to crisis manager centers, in order decisions to be taken, by using risk analysis software. In Figure 4, the above mentioned integrated system is presented. More details are available on [www.unisdr.org/ppew/news/compendium-ewp.pdf](http://www.unisdr.org/ppew/news/compendium-ewp.pdf).

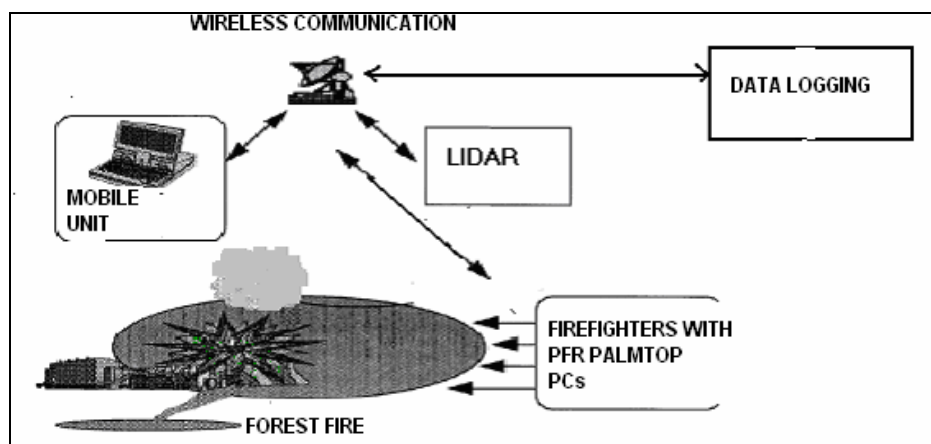


Figure 4. Integrated system for air-quality monitoring in a forest fire.

### ➤ Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) for chemical analysis of particles

(E. Filimundi, TSI Inc., Fr)

#### 1. Introduction

The Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) is a revolutionary instrument in the field of analytical chemistry, based on an instrument built by Prof. Kimberly A. Prather and her associates at the University of California, Riverside (E. Gard, Anal. Chem. 69 (1997) 4083). ATOFMS can be moved between measurement sites with minimal set-up or reconfiguration. ATOFMS instruments offer great potential in areas, such as atmospheric science, biological detection, pharmaceutical manufacturing and engine research.

## 2. Aerosol Time-of-Flight Mass spectrometers with aerodynamic focusing lens technology

ATOFMS with aerodynamic focusing lens technology identifies the specific chemical compounds that produce each particle. Thus, new insights into the dynamic chemistry between particles and surrounding gases are offered, along with other particles. Nearly immediate composition analysis eliminates problems associated with traditional aerosol sampling onto a filter or impactor plate, such as, possible secondary chemical reactions or losses of semivolatile compounds.

### 2.1. Compound analysis

Fragments of inorganic compounds, formed during the ionization process, are commonly made up of single elements and molecular ions, as well as, cluster ions in an oxygen-rich atmosphere, containing one or two elements and oxygen. Many organic compounds provide positive mass spectra, similar to those found in libraries of 70-eV electron impact (EI) mass spectrometry (P.J. Silva et al., Environ. Sci. Technol., 33 (1999) 3068). Negative mass spectra of organic compounds largely show carbon cluster fragments and contain fragments indicating the presence of electronegative ions, such as oxygen and nitrogen.

Many polyaromatic hydrocarbons (PAHs) have a large absorption cross-section because 266-nanometer light induces a resonant process. This leads to high sensitivity when compared to other organic compounds. The detection limit for PAHs is at the range of  $10^{-18}$  mol (B.D. Morrical et al., J. Am. Soc. Mass Spectrom. 9 (1998) 1068). Extensive fragmentation results in difficulties to distinguish compounds in a particle, which contains many organics.



Figure 1. ATOFMS shown without Aerodynamic Focusing Lens installed.

However, it is often possible to determine specific classes of particles (PAHs, aliphatics, organic acids) based on a fingerprint or combination of peaks. The bipolar ion-analysis capabilities of ATOFMS enhance the identification of several specific classes of compounds, such as, organic acids and salts.

## **2.2.Applications**

ATOFMS instruments determine single particle size and chemical composition in near real-time. Applications include:

- Analytical aerosol research.
- Atmospheric particle characterization, such as emission source identification.
- Semiconductor processing.
- Hard-disc-drive crash tests.
- Indoor-air-quality monitoring.
- Aerosolized-drug-delivery research.
- Inhalation toxicology studies.
- Drug-enforcement sample analysis.
- Chemical and biological aerosol detection.
- Engine emission measurements.
- Powder manufacturing quality and process control for pigments, ceramics, polymers, pharmaceuticals, toners and food powders.

### **➤ Experimental study on response sensitivity of smoke detectors in different flow velocities**

*(Zhang YongMing, Liu Naian and Xie Qiyuan, State Key Laboratory of Fire Science, University of Science and Technology, Ch)*

## **1.Introduction**

Early detection of smoke is critical, in order to achieve early suppression of fire and prevent its expansion. Smoke detectors performance can be affected by various parameters, such as wind velocity. This presentation is an experimental study of the performance of two types of detectors (photoelectric and ionization smoke detectors), in a Fire Emulator/Detector Evaluator (FE/DE) that emulates fire-scenarios. The first part of the presentation describes the experimental apparatus used and the second part presents a number of experiments concerning the response sensitivity of the smoke detectors in different flow velocities.

## 2.Fire Emulator/Detector Evaluator (FE/DE)

### 2.1.Concept of the FE/DE

The FE/DE has been designed to emulate a wide range of fire and non-fire scenarios to which a spot-type fire detector could be exposed and evaluated. This approach is quite important, not only for the engineering application but also for the development of the new fire detection technology. More specifically, the FE/DE is a flow tunnel, designed to reproduce the time-varying temperature, flow velocity and particulate concentration or gas concentration expected at detector locations in the early stages of the fire.

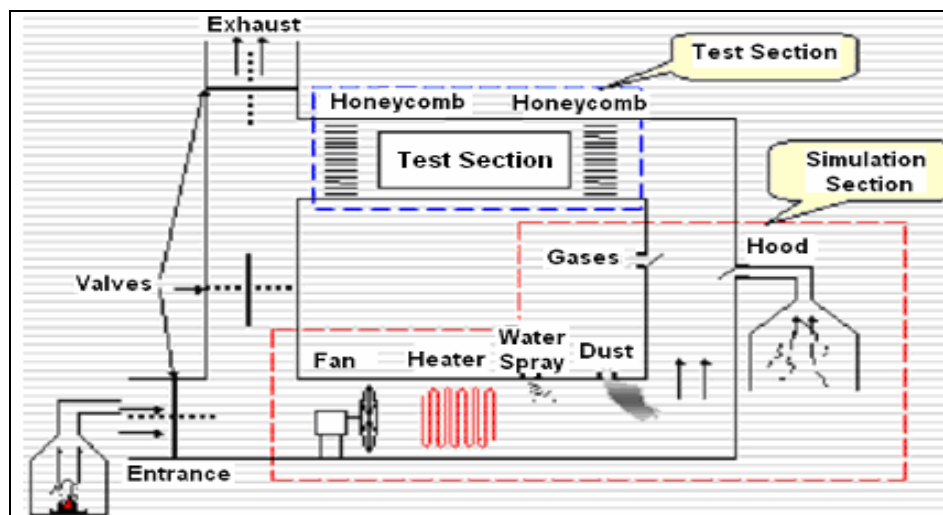


Figure 1. Schematic diagram of the FE/DE.

In Figure 1, the schematic diagram of the FE/DE (State Key Laboratory of Fire Science in China) is presented. It is a circle flow tunnel with three big valves. Along the tunnel, there are the axial blower, the electrical heater, the water spray, the dust feeder and a hood. In addition, the smoke or other aerosol can be drawn into the tunnel directly from the entrance of the FE/DE or by using the smoke-generating box. Since real fire signals or nuisance sources can be simulated with those parts, they constitute the so-called “**simulation section**”. Finally, the simulated aerosol arrives at the “**test section**”, where the fire detectors are evaluated. More specifically, the two sections of the FE/DE are aparted from:

1. *Simulation Section*: Fan (controlled by a transducer), heater, water spray, dust feeder, gases inlet.
2. *Test Section*: Detectors, thermal resistance, humidimeter, air flow velocity probe.



In Figure 2, a photograph of FE/DE simulator with its compartments is given.

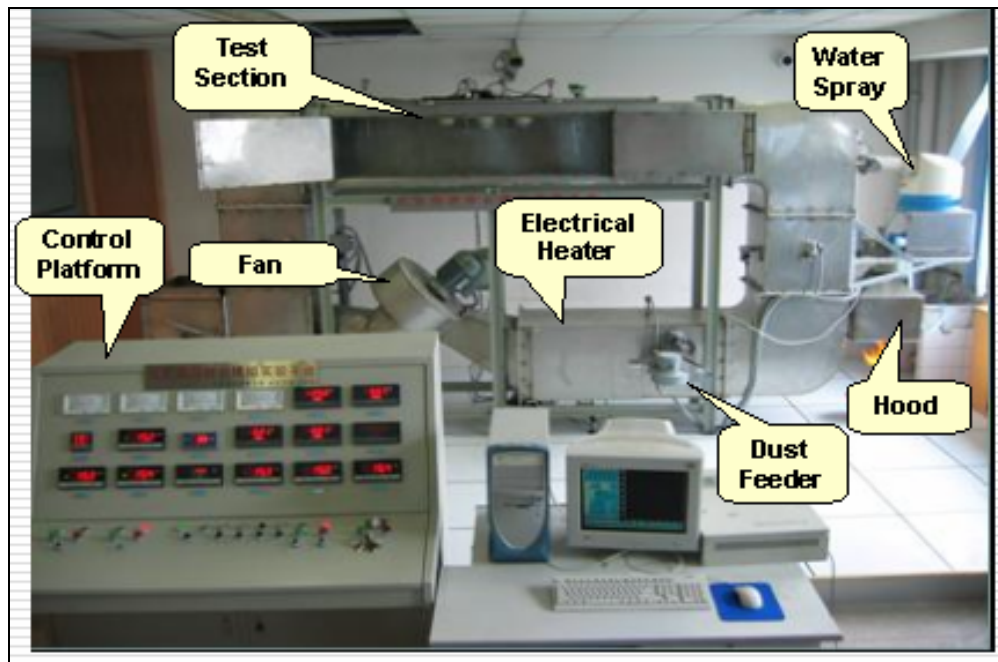


Figure 2. FE/DE simulator with its compartments (photograph).

## 2.2.Details of test section-components

The components of the FE/DE are spot-type fire detectors and the corresponding measuring equipments.

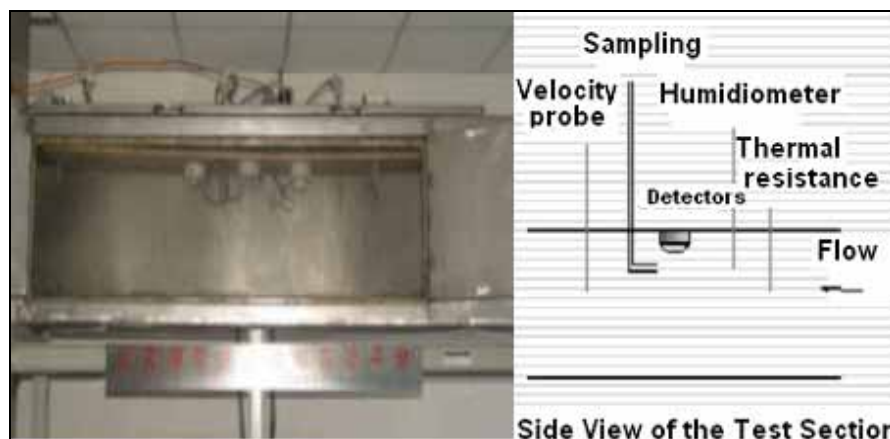


Figure 3. Schematic diagram and photograph of the Test Section.

In Figure 3, the detail schematic diagram and a photograph of the test section are given. It can be seen that the fire detectors for evaluation are sited under the ceiling of the tunnel and that the thermal resistance, the humidimeter and the velocity probe, are located around the fire detectors, in order to measure the corresponding fire parameters.

### **3.Experiments**

The experiments took place in order to evaluate the response sensitivity of two types of smoke detectors in different flow velocities, based on whether the smoke generation was influenced by flow velocity or not. The two experiment series included smoldering cottons that were put in the smoke-generating box and smoldering cottons that were put at the entrance of FE/DE.

#### **3.1.Experiment series-1**

It was found that when the smoldering cottons were put in the smoke-generating box, the process of smoke generation was not influenced by the flow velocity. For those series, eleven experiments took place with the flow velocity at the test section from 0.5m/s to 5.5m/s, using 60 smoldering cottons as smoke source in the box. For every experiment, the digital outputs from the photoelectric and ionization smoke detectors were recorded for analysis.



*Figure 4. 60 smoldering cottons put in the smoke-generating box.*

The response outputs of photoelectric and ionization smoke detectors in flow velocities between 1.0-3.0 m/s and under the experimental conditions described above, are presented in Figures 5-7. The increments of outputs of the two types of smoke detectors are also indicated in Figure 8.

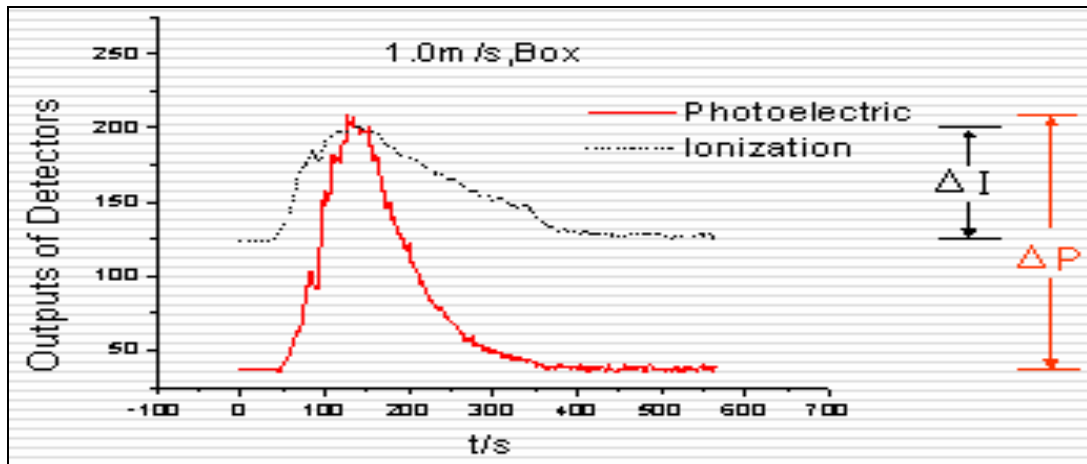


Figure 5. Outputs of detectors for 1.0 m/s flow velocity, when 60 smoldering cottons are used as smoke source in the box.

More specifically, in Figure 6, the response outputs of two kinds of smoke detectors with the flow velocity in the test section 2.0 m/s, are shown. Compared with the corresponding outputs in Figure 5, it is clear that the increments of both smoke detectors decreased.

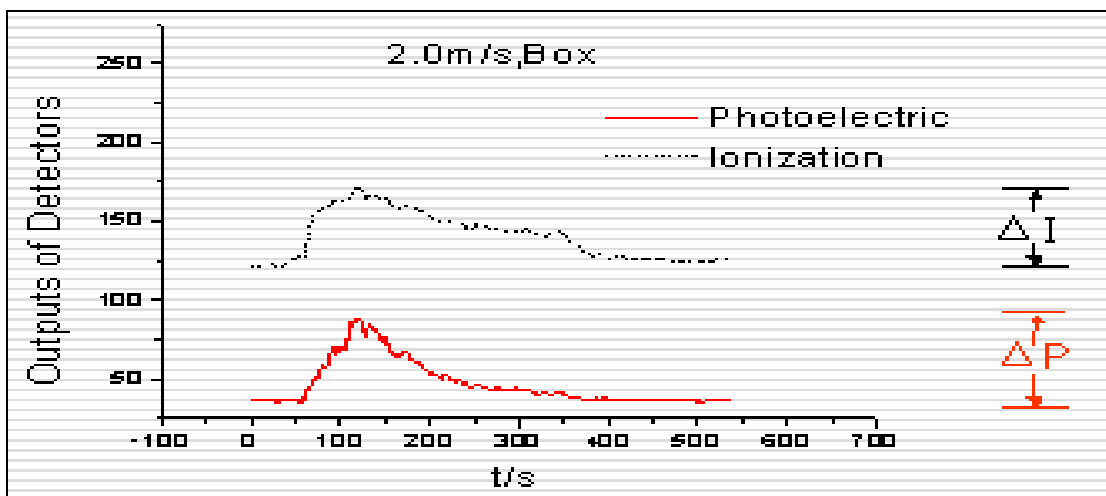


Figure 6. Outputs of detectors for 2.0 m/s flow velocity, when 60 smoldering cottons are used as smoke source in the box.

In Figure 7, the response outputs of two detectors with the flow velocity at 3.0 m/s are shown. It can be seen that both increments still decreased along with the increasing of the flow velocity. Under this condition, it can be said that the response sensitivity of the two smoke detectors decreased as the flow velocity increased. This can be seen more clearly in Figure 8.

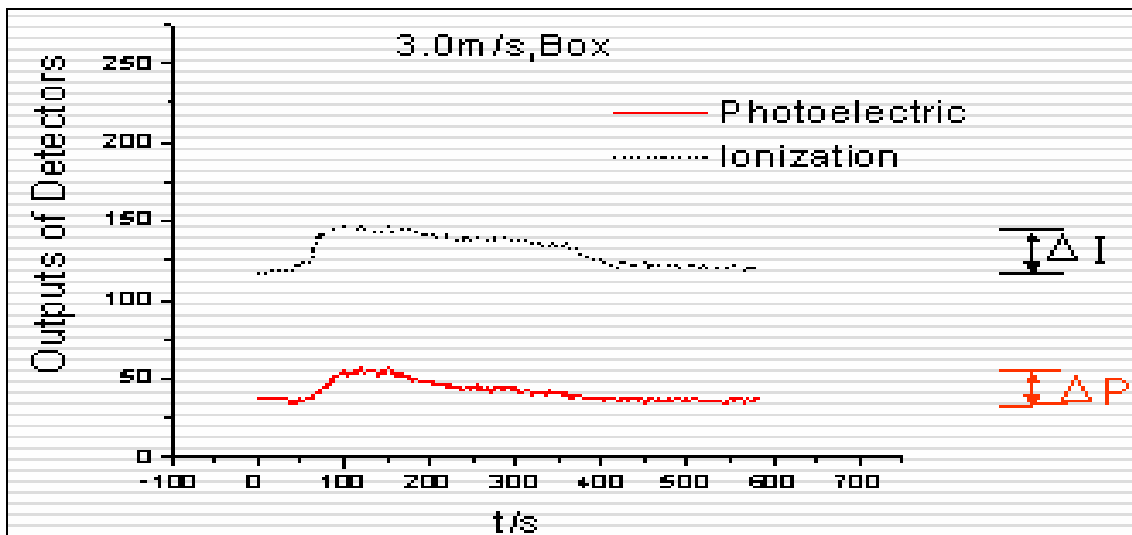


Figure 7. Outputs of detectors for 3.0 m/s flow velocity, when 60 smoldering cottons are used as smoke source in the box.

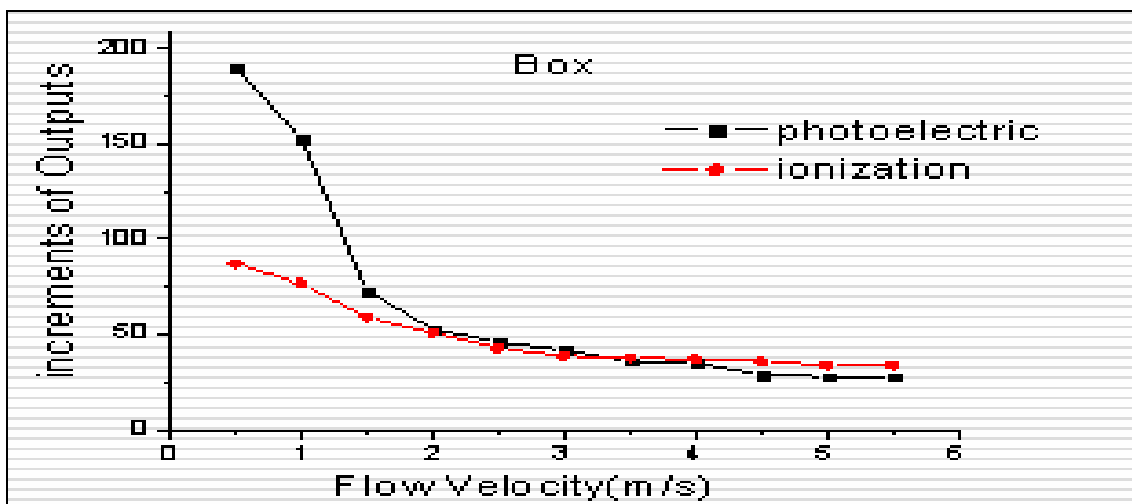


Figure 8. Increments of outputs of the two smoke detectors in different flow velocities (with the 60 smoldering cottons in the box).

### 3.1.1.Discussion-1

Firstly, it seems that since the smoldering cottons were put in the box, the smoke generation was not influenced by the flow velocity in the tunnel. In addition, among the eleven experiments, both the amount and size distribution of smoke particles released from the box was the same. Finally, the main effect of different flow velocity on the response of two kinds of smoke detectors was the different dilution of smoke density in the tunnel.

### 3.1.2.Preliminary conclusions-1

It can be seen that the response values of the two smoke detectors decreased as the flow velocity increased.

### 3.2.Experiment series-2

In those experiments, 60 smoldering cottons were put directly at the entrance of the FE/DE flow tunnel. As long as the process of smoke generation was influenced by the flow velocity in the tunnel the amount and the size distribution of smoke particles were different under the conditions of different flow velocities. Eleven experiments were also conducted, as for the experiment series-1, with the flow velocity in the test section from 0.5 to 5.5 m/s.

In Figures 9, 10 and 11, the outputs of the two types of smoke detectors with the flow velocity set at 1.0, 2.0 and 3.0 m/sec respectively, are shown.

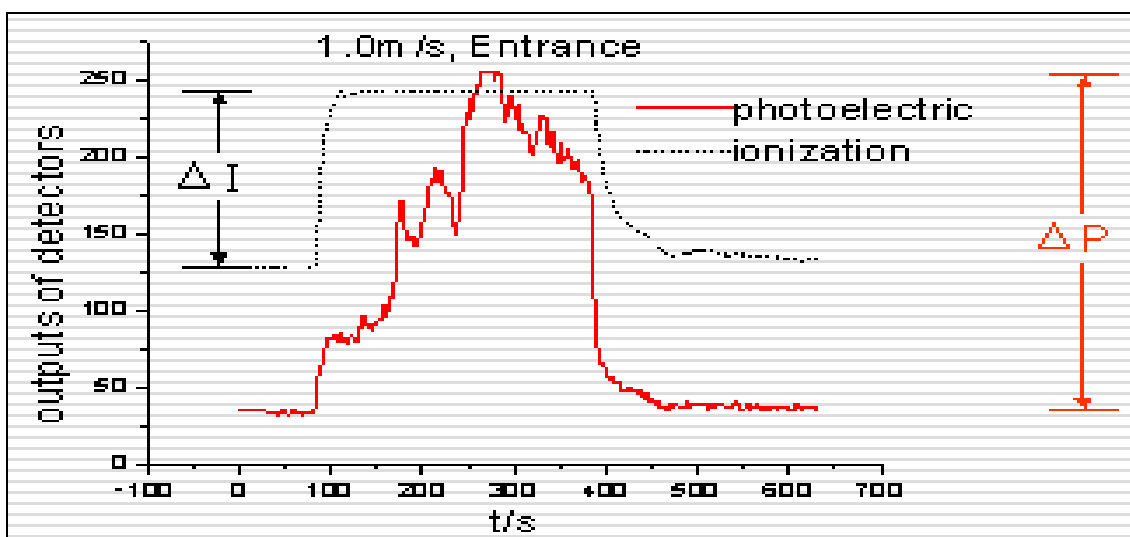


Figure 9. Outputs of detectors for 1.0 m/s flow velocity, when 60 smoldering cottons are put directly at the entrance of the FE/DE.

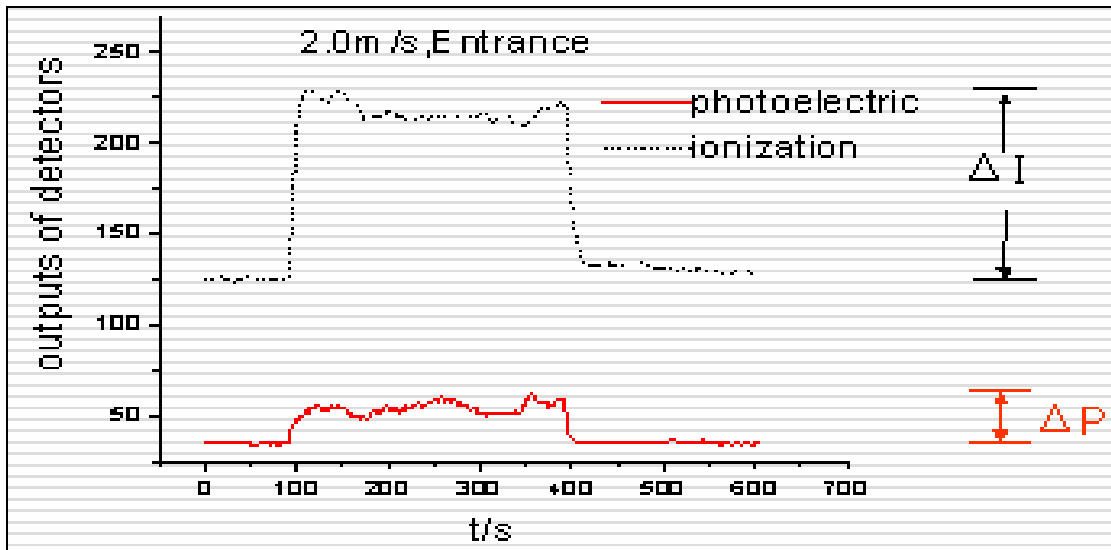


Figure 10. Outputs of detectors for 2.0 m/s flow velocity, when 60 smoldering cottons are put directly at the entrance of the FE/DE.

According to Figures 9 and 10, it can be concluded that only the increment of output of the photoelectric smoke detector decreased when the flow velocity in the tunnel increased from 1.0 to 2.0 m/sec. Though, it seems that the corresponding increment of ionization smoke detector was little decreased. This trend can be seen more clearly in Figure 11, where the increment of photoelectric smoke detector decreased further when the flow velocity increased to 3.0 m/sec, whereas the increment of ionization smoke detector was little decreased.

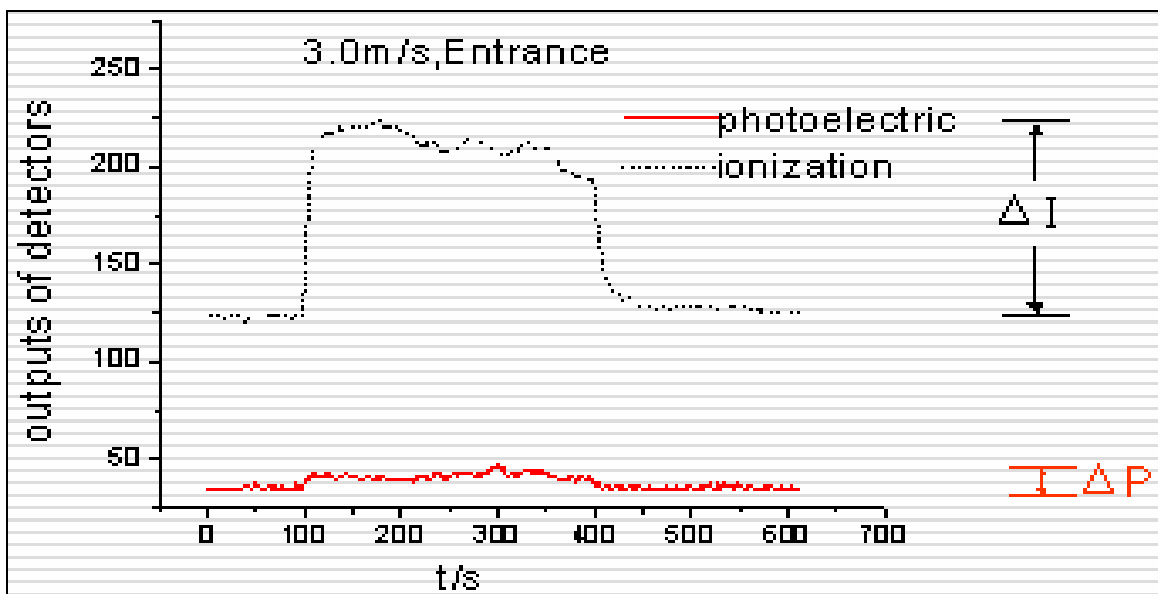


Figure 11. Outputs of detectors for 3.0 m/s flow velocity, when 60 smoldering cottons are put directly at the entrance of the FE/DE.

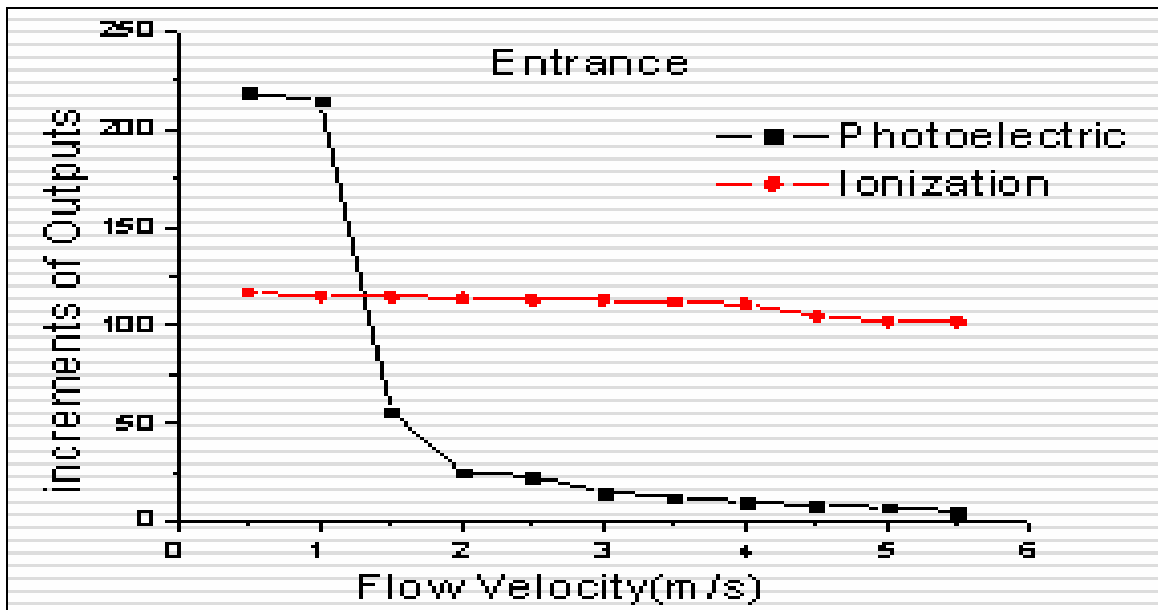


Figure 12. Increments of outputs of the two smoke detectors in different flow velocities, with the 60 smoldering cottons put directly at the entrance of the FE/DE.

Emphasis should also be given to the change of outputs increments of the two smoke detectors in different flow velocities, as it is shown in Figure 12. It is clear that the increments of photoelectric smoke detector decreased when the flow velocity in the tunnel increased. Regarding ionization detector, it seems that the corresponding increments little decreased and almost remained at a certain value. The trend of increments of outputs is quite different from that of experiment series-1.

### 3.2.1. Discussion-2

It was observed that the amount of smoke particles produced increased along with the flow velocity increase. The mean diameter of particles decreased along with the flow velocity increase. For that reason increased flow velocities were tested in the tunnel.

### 3.2.2. Preliminary conclusions-2

Ionization smoke detectors seem to be more responsive (sensitive) to smaller smoke particles than photoelectric detectors. According to the above experiments, ionization smoke detectors show better response sensitivity in high-flow velocity (small smoke particles) than photoelectric detectors, as soon as, their signal output was not decreased significantly with velocity increase.



## ***Session 2: Exposure to forest fire smoke (ffs) components and personal protective equipment***

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This session includes presentations referred to specific methods that are used for assessing exposure to forest fire smoke (ffs). Human exposure to smoke pollutants, such as particles and their possible adverse health effects, are discussed. Specifications of personal protection means for the fire-fighters are also presented.

### **➤ Measurement and modeling of exposure to air toxic concentrations for health effect studies: MATCH**

***(S. Vardoulakis, University of Birmingham, Division of Environmental Health and Risk Management School of Geography, Earth and Environmental Sciences, UK)***

#### **1.Introduction**

Until now, although the study of personal exposure to air pollution is a rather well developed science, it has been restricted to a relatively limited range of pollutants. In addition, there has been little verification of personal exposure models by personal samplers. This study aims at leading to major advances in understanding the causes and magnitude of exposures to relevant air toxics substances. Moreover, it intends to comment on whether collecting lifestyle information, compared with exposures evaluated independently by personal samplers for a range of air toxics substances, is sufficient to model personal exposures reliably.

#### **2.MATCH project overall aim**

The overall aim of the MATCH project is to:

- Quantify the magnitude and range of individual personal exposures to 16 Volatile Organic Compounds (VOC), including 1,3-butadiene and 21 Polycyclic Aromatic Hydrocarbons (PAHs).
- Develop models for exposure prediction, based upon time/activity diaries and micro-environmental concentrations.

### **3.MATCH methodology**

Exposure assessment of subjects took place by carrying out different types of measurements and procedures, as shown below:

#### **a.Personal exposure (PE) measurements**

- *100 healthy adult volunteers.*
- *Target pollutants: 16 VOC (including 1,3-butadiene), 21 PAHs.*
- *Urine samples: benzene and Environmental Tobacco Smoke (ETS) biomarkers.*

#### **b.Micro-environmental (ME) measurements**

- *Indoor, (home, office, pub, restaurant, railway station, etc.).*
- *Outdoor, (street canyon, shopping area, park, etc.).*
- *Transient, (car, train, bus).*

#### **c.Personal exposure modeling**

- *Using personal exposure concentrations.*
- *Micro-environmental concentrations.*
- *Time/activity diaries.*

#### **d.Model validation**

- *Using personal exposure concentrations (independent data-set).*
- *Biomarker data, (ETS and benzene).*

#### 4. MATCH project outline

The MATCH project consists of the phases shown in Figure 1:

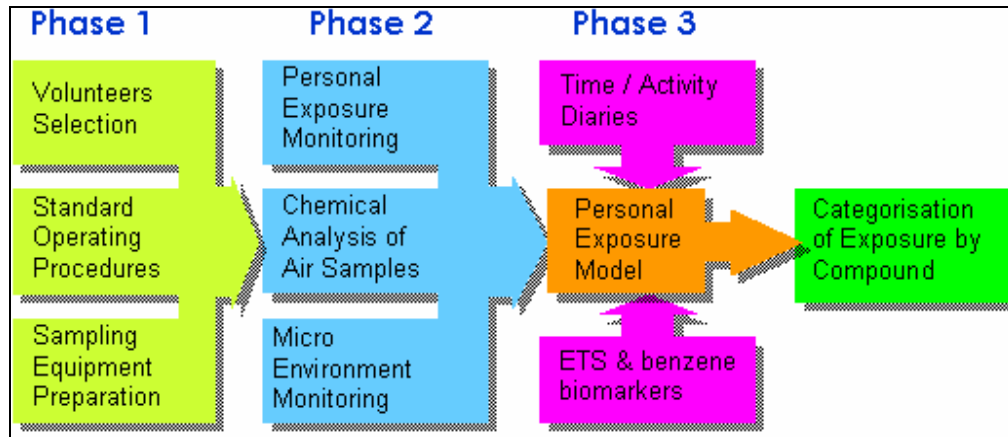


Figure 1. Phases of the three-year MATCH project

#### 5. MATCH sampling strategy

Samples were taken according to specific strategy and hence, the selected micro-environments (ME) were:

- Representative indoor, outdoor and transient ME.
- In urban, sub-urban, rural areas.
- Account for spatial variability of air pollution.

For the selection of volunteers the parameters that were taken into consideration were to have:

- Statistically representative group.
- Wide range of exposures (but not occupational).
- Diverse lifestyles.
- Non-smokers (but possibly exposed to ETS).

The sampling periods were:

- 5 days x 24 hour integrated personal exposure samples.
- 8 - 12 hour integrated indoor microenvironment samples.
- 2 - 4 hour integrated outdoor microenvironment samples.
- Balanced over all seasons of the year.
- Weekdays (95%) and weekends (5%).

Percentages of the selected micro-environments are presented in detail in Figure 2 and occupational categories of suitable volunteers for the MATCH study are given in Figure 3.

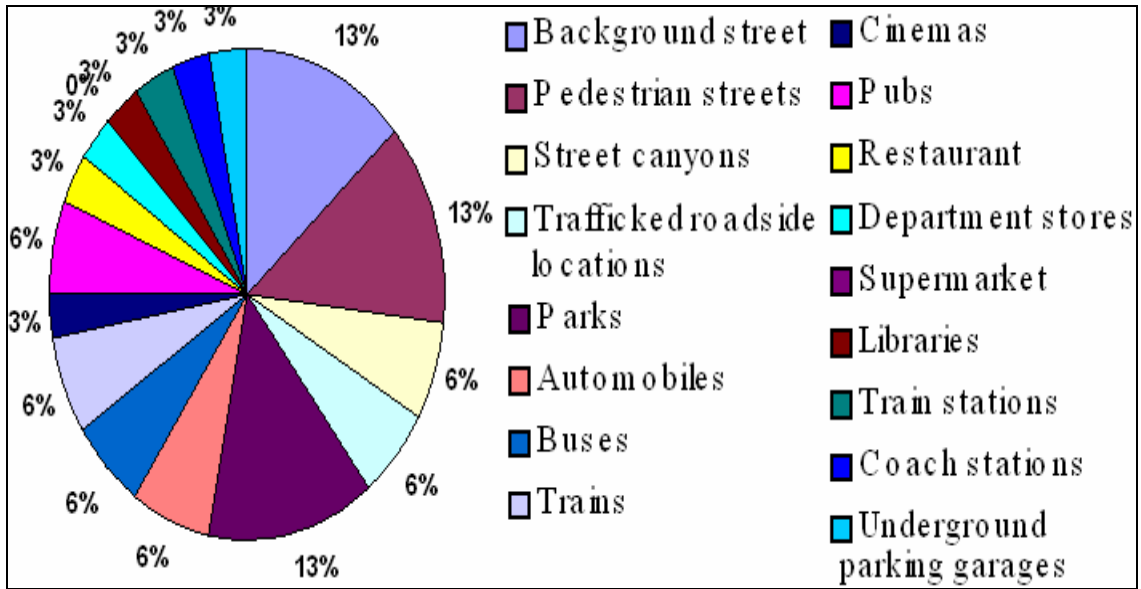


Figure 2. Percentage of microenvironments selected for the MATCH study.

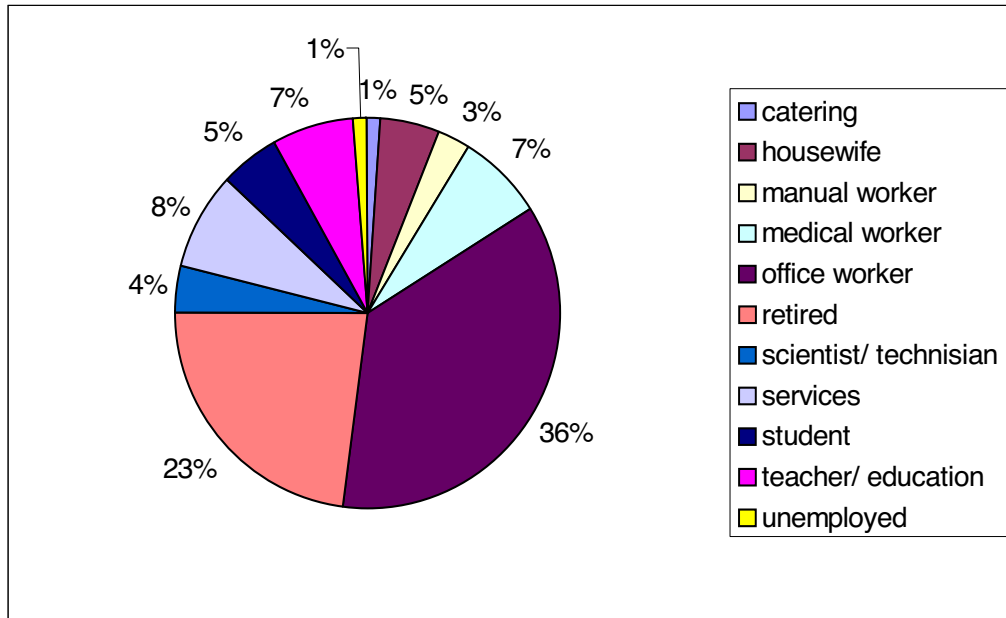


Figure 3. Occupational categories of suitable volunteers for the MATCH study.

## 6.MATCH sampling locations

In Figure 4, a map is presented, where the locations selected for sampling are indicated. More specifically, MATCH sampling locations were London (Urban hotspots), West Midlands (Urban area, Suburban areas) and South Wales (Rural area, Industrial area).

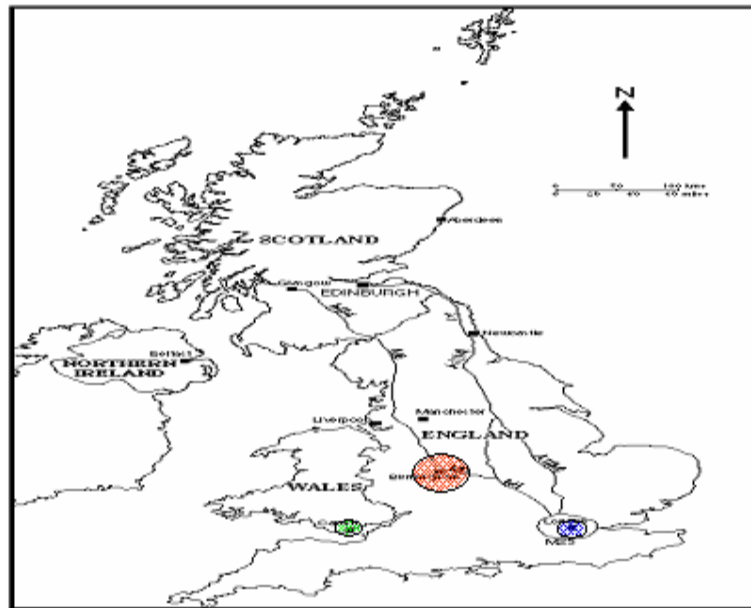


Figure 4. MATCH sampling locations.

## 7.MATCH sampling equipment

The equipment used is shown in Figures 5 and 6:

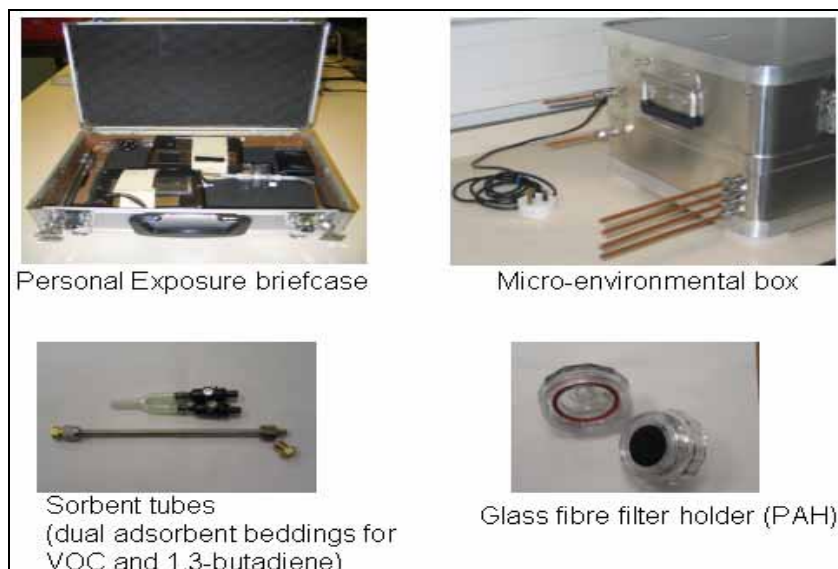


Figure 5. MATCH sampling equipment.



*Figure 6. Personal exposure briefcase used for air sampling in micro-environments of the volunteers.*

### **8.MATCH analytical method**

The analytical methods used for identification of air pollutants are shown in Figure 7. More specifically:

1. Volatile Organic Compounds and 1,3-butadiene were identified by:

- Thermal Desorption.
- GC/MS analysis.

2. Polycyclic Aromatic Hydrocarbons (PAH) were identified by:

- Accelerated Solvent Extraction.
- GC/MS analysis.



*Figure 7. Analytical equipment for VOCs and PAHs analysis.*

## 9.MATCH progress (first year)

The MATCH project had achieved the first year:

- Standard Operating Procedures for sampling and analysis.
- Sampling equipment built in-house.
- About 20% of total air samples collected and analysed.

Figure 8, shows benzene concentrations for three volunteers living in different locations, i.e. in urban, sub-urban and rural areas, in West Midlands. The box plots (PE, Personal Exposure) show the range of personal exposures to benzene (24-hour averages) over a period of five days, while the single lines (HD, Home Day Microenvironment, HN, Homenight Microenvironment, W, Working) represent benzene concentrations in two different indoor micro-environments (12-hour averages at homes during day-time and night- time and 8-hour averages in offices).

These initial results provide some evidence that personal exposure to benzene can be partly re-constructed from measurements taken in homes and offices. However, representative measurements from other indoor, outdoor and transient micro-environments (e.g. street canyons, cars, buses, railway stations, supermarkets, pubs, etc.) are needed, in order to model personal exposure reliably, using time-activity diaries.

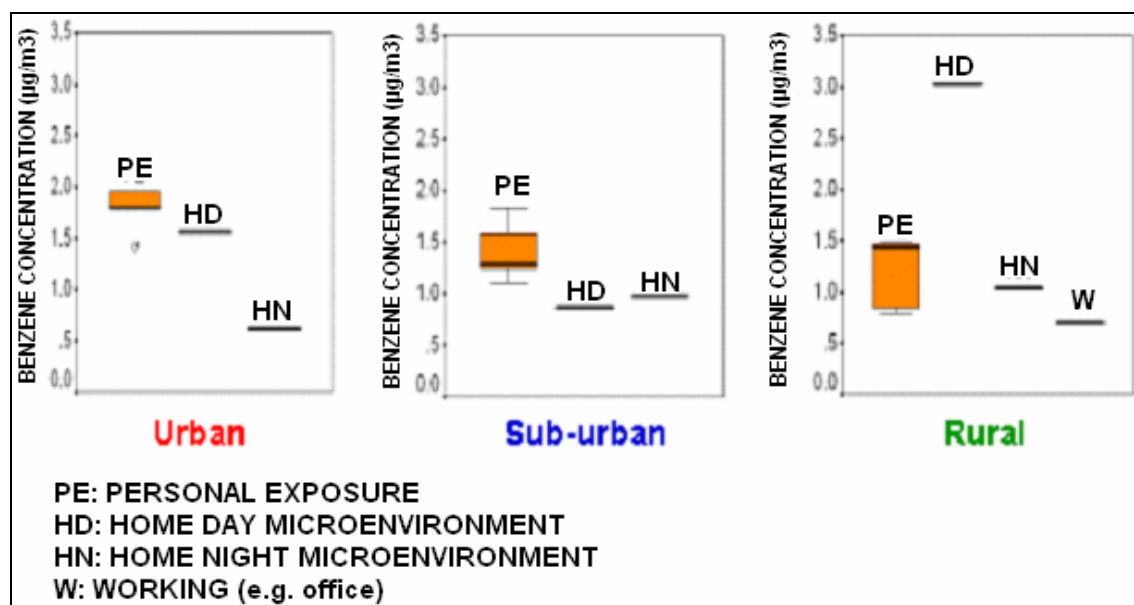


Figure 8. Benzene concentrations for 3 volunteers in different micro-environments.



## 10.MATCH future work

Future work includes the sampling and analysis of the following compounds during the second and third year of the project:

- VOCs and 1,3-butadiene.
- Polycyclic Aromatic Hydrocarbons (PAHs).
- Nicotine, cotinine, and benzene biomarkers (in urine samples).

This sampling will cover a variety of personal exposure patterns, as well as, representative indoor, outdoor and transient micro-environments.

## 11.Exposure modeling

A statistical model will be developed, which will allow an estimate of overall daily personal exposure that can be compared with exposure measured by the personal monitor. Further statistical analysis of the experimental datasets will reveal groups of substances from common origin and volunteers with similar exposure patterns.

- **Statistical modeling:**

$$Personal\ Exposure = \frac{\sum C_m \cdot T_m}{Total\ Time}$$

where,

**$C_m$**  = micro-environment concentration.

**$T_m$**  = time spent in micro-environment  **$m$** .

- **Principal Component Analysis (PCA):** in order to identify groups of substances from common source.
- **Cluster Analysis:** in order to identify subjects with similar exposure patterns.

## 12.Model validation

The personal exposure model will be tested to verify its reliability in predicting personal exposures, by using an independent set of personal exposure data on a smaller number of subjects. This may reveal limitations of the model that may possibly be surpassed by the specific modifications.

### **13.MATCH information**

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<http://www.gees.bham.ac.uk/research/match/>

#### **MATCH research team**

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#### **➤Exposure limits for particles**

**(G. Seynaeve, Ministry of Health, WADEM, Be)**

#### **1.Introduction**

Particles are considered a major product of forest fuel combustion and can cause various adverse health impacts on the exposed population. This presentation includes general principles and information regarding airborne particles absorption by human body and their possible toxicity when inhaled. Exposure limits for particles, established by various organizations, are also discussed.

#### **2.Toxic effect of particles**

Particles can absorb toxic or reactional substances, (e.g. active metabolites, free radicals). Toxic effect of particles is related to:

- a. The quantity of toxic or reactional substance.
- b. The affinity for site of action (enzyme, membrane, motor plate, receptor).

### **2.1. Concentration of active toxic at site of action**

When particles are inhaled, their concentration of active toxic at site of action is because of biological:

- Absorption.
- Distribution.
- Transformation.
- Excretion.

### **2.2. Biological absorption and excretion of particles**

In general, biological absorption of particles by human body can take place by filtration through pores of membranes, simple diffusion, facilitated diffusion, active transport (against concentration gradient) or endocytose (pinocytose – phagocytose) e.g. asbestos fibres that are absorbed by macrophages. Biological absorption can be oral (mouth, stomach, intestine, colon), pulmonary, cutaneous (skin), ocular (eyes) or parenteral.

More specifically, oral absorption can take place:

- a. secondary, by inhalation or swallow,
- b. as contaminated food/drinks,
- c. via smoking, e.g. heavy metals dust (Pb, As, Cd) (H. Roels, Am J Ind Med, 3 (1982) 53).

Cutaneous absorption can be:

- a. trans-epidermic.
- b. pilosebaceous (hair follicles, sebum & sweat glands).

### **2.3. Health effects in general**

The general health effects due to particles can be:

- Acute toxicity.
- Skin corrosion/irritation.
- Serious eye damage/eye irritation.
- Sensitisation (allergy).
- Germ cell mutagenicity.
- Reproductive toxicity.
- Carcinogenicity.
- Specific target organ systemic toxicity (TOST).
- Respiratory irritation.
- Water activated toxicity/corrosion.

- Narcotic effects.
- Aspiration hazard.
- Immunotoxicity.

In Table 1, classification criteria for acute toxicity are shown.

*Table 1. Classification criteria for acute toxicity*

<b>Acute toxicity</b>	<b>Cat. 1</b>	<b>Cat 2.</b>	<b>Cat. 3</b>	<b>Cat. 4</b>	<b>Cat.5</b>
					<b>Criteria:</b>
<b>Oral (mg/Kg)</b>	5	50	300	2.000	-Anticipated oral LD50 between 2000 and 5000 mg/kg.
<b>Dermal(mg/Kg)</b>	50	200	1000	2000	-Indication of significant effect on human.
<b>Gases(ppm)</b>	100	500	2500	5000	-Significant clinical signs at class 4.
<b>Vapours(mg/L)</b>	0.5	2.0	10	20	- Indications from other studies.
<b>Dusts and mists (mg/L)</b>	0.05	0.5	1.0	5	

### 3.Types of airborne contaminants

The types of airborne contaminants can be:

- *solid aerosols*
  - dusts, fumes, smoke.
  - particles of < 100 µm in diameter.
- *liquid aerosols*
  - mists, fog.
- *gases & vapors.*
- *bio-aerosols.*
  - live agents or products of live agents.

#### 3.1.Inhaling of airborne contaminants

The possible effects by inhaling airborne contaminants can be:

- a. Direct toxic action on respiratory system (symptoms of irritation: sneezing, coughing, chest tightness, difficulty in breathing; in long term period can cause chronic lung disease i.e. chronic bronchitis, emphysema, asthma, asbestose, silicose, carcinoma, mesothelioma).
- b. Possible penetration in blood circulation of a fraction.

The surface pulmonary alveoli is 80 m<sup>2</sup>, the wall thickness is 0,1 to 0,5 μm and the respiratory volume in a normal workday is 10 m<sup>3</sup>. The factors, which contribute to the specific effects, can be:

- Concentration of airborne contaminants in air.
- Time of exposure.
- Multiple factors such as, gas and vapours (absorption) and aerosols (deposition, clearance/elimination, retention of particles).

### 3.2. Deposition of aerosols in respiratory tree

Deposition of aerosols in respiratory tree (Figure 1), can be affected by factors such as:

1. Physical characteristics of particles (e.g. diameter and form).
2. Anatomical structure of particles.
3. Respiratory parameters (frequency, minute volume).

Retention is defined as the deposition minus the clearance.

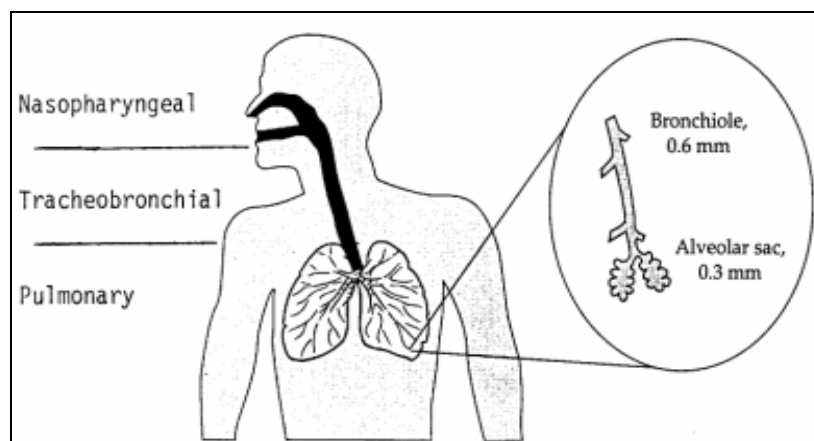


Figure 1. Task Group on Lung Dynamics: three compartments of the Human Respiratory System: Nasopharyngeal (NP), Tracheobronchial (TB), Pulmonary (Ray, 1995).

### 3.3. Fraction of particles deposited on the three compartments of the human respiratory system versus particle diameter

In Figure 2, deposition of particles on Pulmonary, Nasopharyngeal (NP) and Tracheobronchial (TB) compartments of the human respiratory system, as function of their mass median aerodynamic diameter (in μm), is shown. Typical pollutant sizes are shown in Table 2.

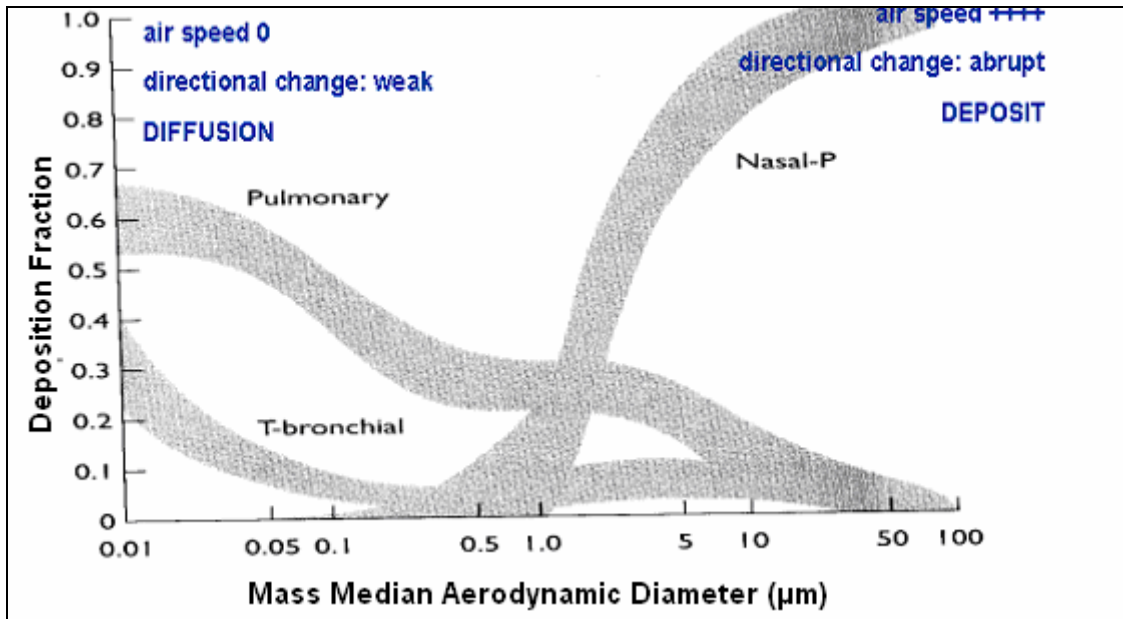


Figure 2. Deposition fraction plotted versus mass median aerodynamic diameter (in  $\mu\text{m}$ ) of particles (Task Group Lung Dynamics, International Commission on Radiological Protection, 1966).

Table 2. Typical Pollutant Sizes.

Pollutants	Sizes
Smoke	0.01 to 1.0 Microns
Bacteria	0.25 to 10 Microns
Human Skin Flakes	0.4 to 10 Microns
Household Dust	0.5 to 100 Microns
Mold	2.0 to 20 Microns
Human Hair	70 to 100 Microns
Pollen	5 to 100 Microns

The particles, according to their size, are categorized as:

- Nano < 100 nanometers.
- Fine > 0.1 – 3 micrometers.
- Respirable (rat) < 3  $\mu\text{m}$ .
- Respirable (human) < 5  $\mu\text{m}$ .
- Inhalable (human) 10 – 20  $\mu\text{m}$  length.

### 3.4. Pulmonary clearance of airborne particles

- Tracheobronchial clearance of airborne particles can take place through:
  - Dissolve in extracellular fluid/mucus layer.
  - Movement cilia & expectoration/ swallowing (modified by inhalation e.g. SO<sub>2</sub>, O<sub>3</sub>, NO<sub>2</sub>, tobacco smoke).
- Pulmonary clearance (respiratory bronchioli & alveoli) of airborne particles can take place through:
  - Movement of liquid/surfactant.
  - Phagocytose by macrophages (lyzosomes or migration).
  - Pinocytose by pneumocytes and phagocytose by interstitial macrophages, or directly in capillary/lymphatic system.
  - Absorption: dissolution and diffusion through alveolar membranes, transferring to blood and ending to target organs without passing liver.

For example, ozone diminishes mobility of pulmonary macrophages.

### 3.5. Absorption of toxic substances

Absorption of toxic substances can be of two types:

#### **A. Type A rapid onset:**

- water-soluble.
- upper respiratory airway.

e.g. HCl, NH<sub>3</sub>, Cl, SO<sub>2</sub>, HF, acrolein (irritant vapours).

*Symptoms: cough, dyspnea, bronchospasm*

#### **B. Type B slow onset of symptoms:**

e.g. Nitric gas, phosgene, Cd-oxide.

*Symptoms: upper and lower airway irritation within 24-hrs.*

### 4. Toxicology: airborne fibers and host reactions

In Figure 3, a dendrogram of particles exposure, dose and response is presented. Information, such as the possible sources of exposure (workplace, ambient air), physicochemical properties of particles (e.g. shape crystalline or amorphous), particle concentration and also human activities/susceptibility, are shown. Moreover, dose characteristics (mechanisms of deposition, clearance /retention) and response characteristics e.g. inflammation, fibrosis, are illustrated.



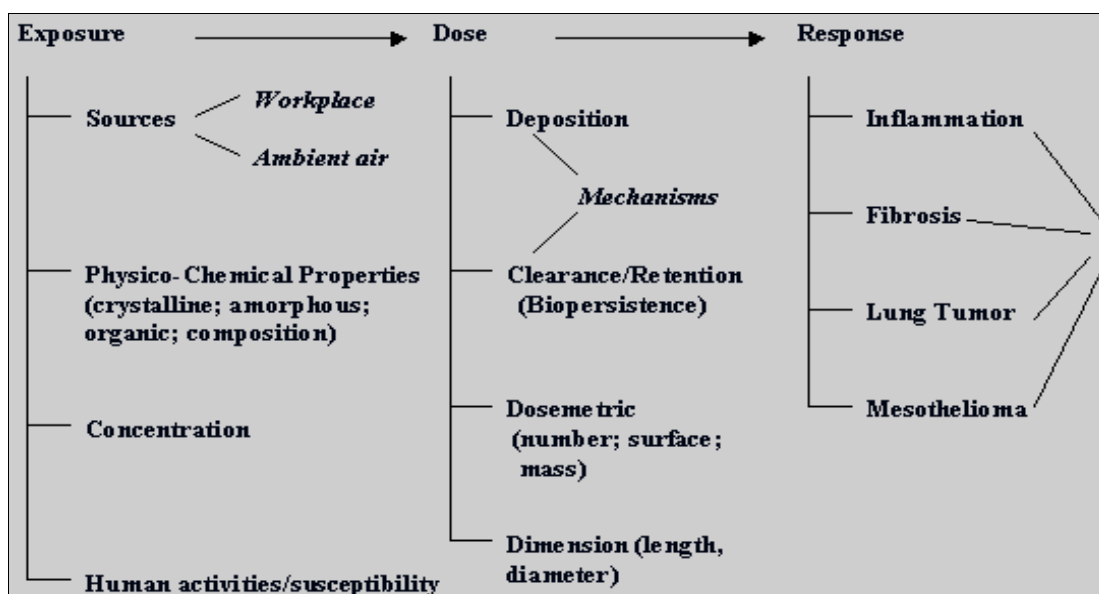


Figure 3. Dendrogram of particles exposure, dose and response.

In Tables 3 and 4, pulmonary inhalation toxicants and systemic inhalational toxicants (asphyxiants, miscellaneous systemic poisons) are presented (e.g. ammonia, formaldehyde, acrolein, aromatic hydrocarbons etc.). In Table 5, some of the common combustion products are shown, such as carbon monoxide, carbon dioxide, phosgene, acetic acid, sulfur oxides, etc.

Table 3. Pulmonary inhalation toxicants.

Irritant Gases			Pulmonary Antigens/ sensitizers	
Upper Airway	Lower Airway	Terminal Airway	Gases/vapors	Dusts (1-5 µm)
Ammonia	Chlorine	Phosgene	Toluene diisocyanate	Bacteria
Sulfur dioxide	Ozone	Nitrogen dioxide	Formaldehyde	Fungi
Hydrogen fluoride			Chlorine	Animal proteins
			Nitrogen dioxide	
Formaldehyde			Ammonia	Plant proteins
Acrolein			Vinyl plastics	Metal

Table 4. Systemic inhalational toxicants.

Asphyxiants		Miscellaneous Systemic Poisons		
Simple	Chemical	Organophosphates	Hydrocarbons	Metal Fumes
Nitrogen	Carbon monoxide	Insecticides	Aromatic-Benzene ring	Beryllium
Methane	Hydrogen cyanide	Nerve gases	Benzene	Cadmium
Carbon dioxide	Hydrogen sulfide	tabun (GA)	Toluene	Mercury
Argon	Methylene Chloride	sarin (GB)	Xylene	Nickel
Helium		soman (gd)	Vinyl Chloride	Vanadium
Nitrous oxide		venom X	Chlorinated	Zinc
Hydrogen			Trichloroethylene	Chromium
			Trichloroethane	Osium

Table 5. Common combustion products.

Carbon monoxide	Hydrogen cyanide	Acetic acid
Carbon dioxide	Phosgene	Formic acid
Chlorine	Nitrogen oxides	Formaldehyde
Hydrogen chloride	Isocyanates	Acroleine
Ammonia	Sulfur oxides	Acetaldehyde

In Table 6, determinants of inhalational pulmonary toxicity are shown, including parameters, such as the pulmonary size, the particle size inhaled and also some water solubility examples. In Table 7, physical asphyxiants are presented, as well as, their possible origin (source) and some of their properties. For example, carbon dioxide can be a by-product of carbohydrate fermentation. It is used in synthesis of urea, in soft drinks, fire extinguishers and it is heavier than air, odourless and non-flammable.

Table 6. Determinants of inhalational pulmonary toxicity.

Pulmonary size	Particle size $\mu\text{g}$	Water Solubility	Examples
Upper airway	> 5	High	Ammonia, sulfur dioxide
Lower airway	1 to 5	Moderate	Chlorine
Terminal airway	< 1	Low	Phosgene, nitrogen dioxide

Table 7. Physical asphyxiants.

Agent	Sources	Properties
Carbon dioxide	By-product carbohydrate fermentation; used in synthesis of urea, in soft drinks, fire extinguishers; dry ice	Heavier than air; odorless; non-flammable
Ethane (Natural gas)	Fuel, freezing agent used in organic synthesis	Heavier than air; flammable
Methane (Natural gas)	Fuel, raw material for production hydrogen, ammonia, acetylene, and formaldehyde	Lighter than air; flammable
Butane (Bottled gas)	Refrigerant, aerosol, organic synthesis, solvent; raw material for automobile fuels	Heavier than air; odor of petroleum or may be scented w/mercaptanes; flammable
Propane (Bottled gas)	Refrigerant, aerosol, organic synthesis, solvent; raw material for fuels	Heavier than air; odor of petroleum or may be scented as mercaptanes; flammable
Liquid petroleum gas	Domestic, industrial and automotive fuel	Heavier than air; flammable
Nitrogen	Manufacturing of ammonia	Lighter than air; inert; non-flammable
Hydrogen	Metallurgy, electric bulbs, plumbing materials, vacuum tubes, glass fusion, oxygen-hydrogen welding procedures	Lighter than air; flammable
Ethylene	Used to mature fruits in manufacturing process of polyethylene, acetaldehyde, ethyl chloride	Lighter than air; sweet odor and taste; flammable
Neon	Used in neon signs	Lighter than air; inert; non-flammable
Argon	Used in neon signs	Heavier than air; inert; non-flammable
Acetylene	Used in welding operations	Lighter than air; slight garlic odor; flammable

## 5. Exposure to airborne contaminants

There is a question raised about the scientific origin of exposure limits and how they have been established. Biological and clinical studies on human or animals, as well as, occupational & environmental epidemiological studies, e.g. exposure to PM<sub>10</sub> and hospital admissions for childhood respiratory illness have been reported that were correlated with political issues (OECD ENV/JM/MONO, Technical guidance document on the use of socioeconomic analysis in chemical risk assessment, 2002).

### 5.1. Environmental epidemiology

Environmental epidemiology includes:

1. The exposure-health chain (Figure 4).
2. Spatial & temporal characteristics of exposure (Figures 5 and 6).
3. Designing an exposure indicator.
4. Case-studies.
5. PM<sub>10</sub> exposure measures.

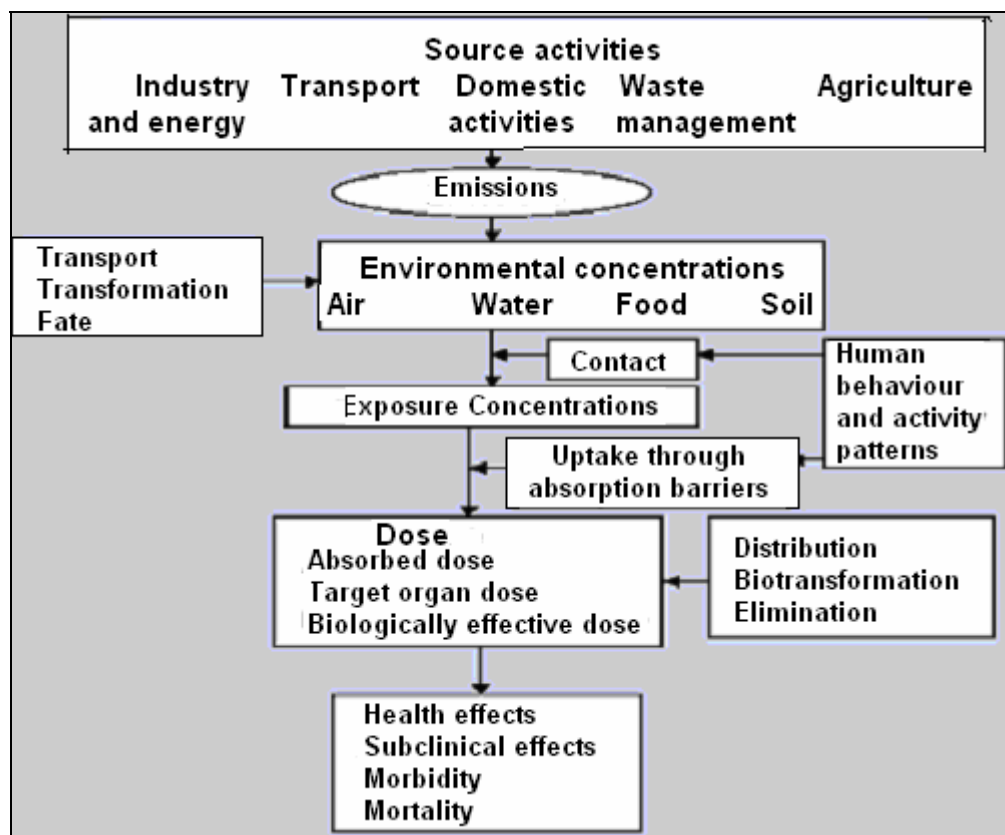


Figure 4. The exposure-health chain.

The exposure – health chain presented in Figure 4, includes parameters, such as the source of activities (industry and energy, transport, domestic activities etc.), the emissions and their environmental concentrations in the air, water, food and soil, as well as, their contact with human. Exposure concentrations, dose and the respective health effects (subclinical effects, morbidity, mortality), are also presented.

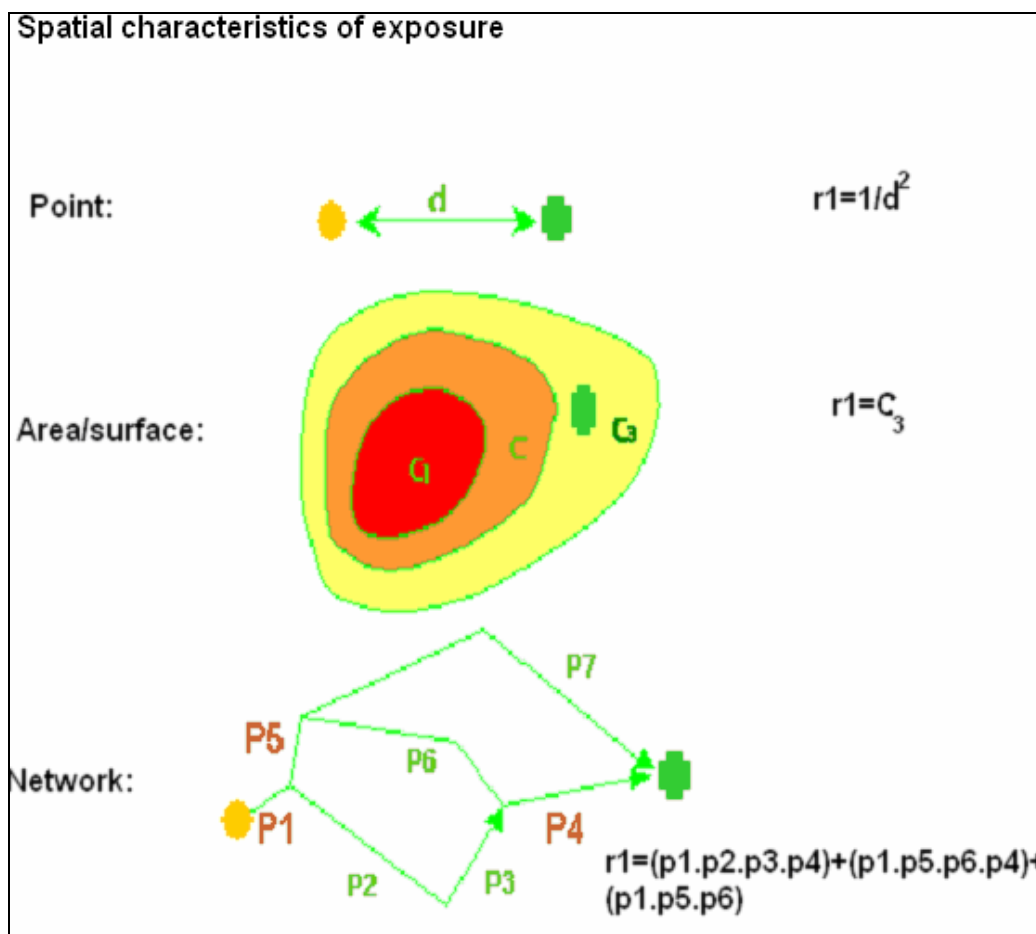


Figure 5. Spatial characteristics of exposure.

According to Figure 5, exposure can be characterized as point, area/surface or network; such exposure characteristics should be taken into account for addressing exposure limits. Temporal, discrete or continuous characteristics of the exposure, as shown in Figure 6, have to be taken into account in order to calculate an averaged, sporadic or cumulative exposure, respectively. In Figure 7, the temporal relationship exposure versus the possible health effects, are shown.

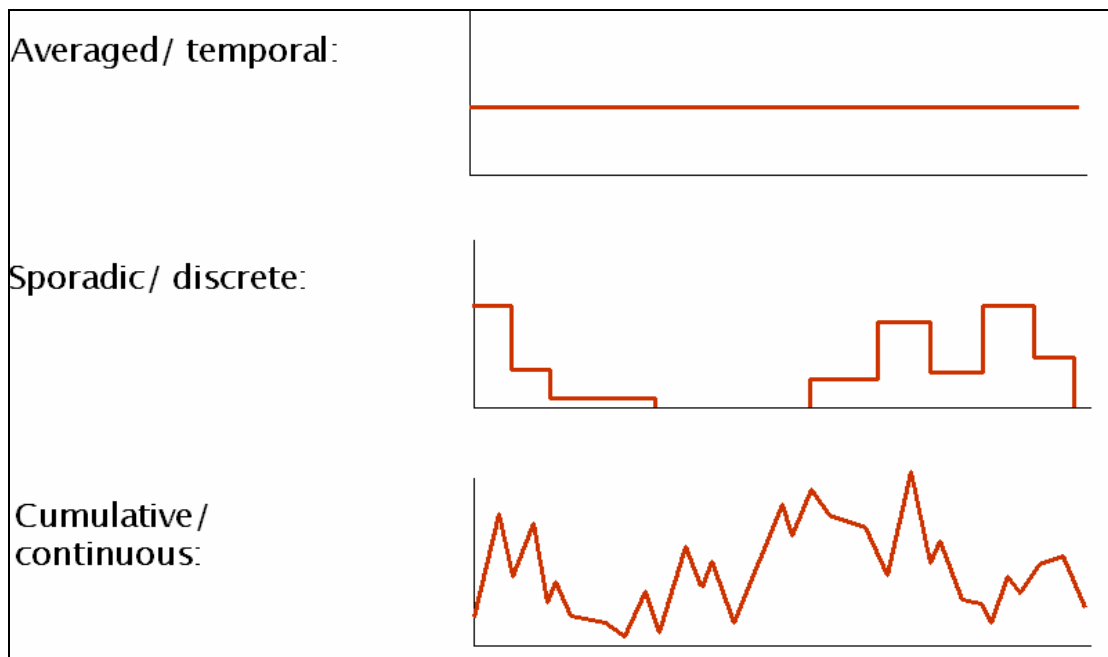


Figure 6. Temporal characteristics of exposure.

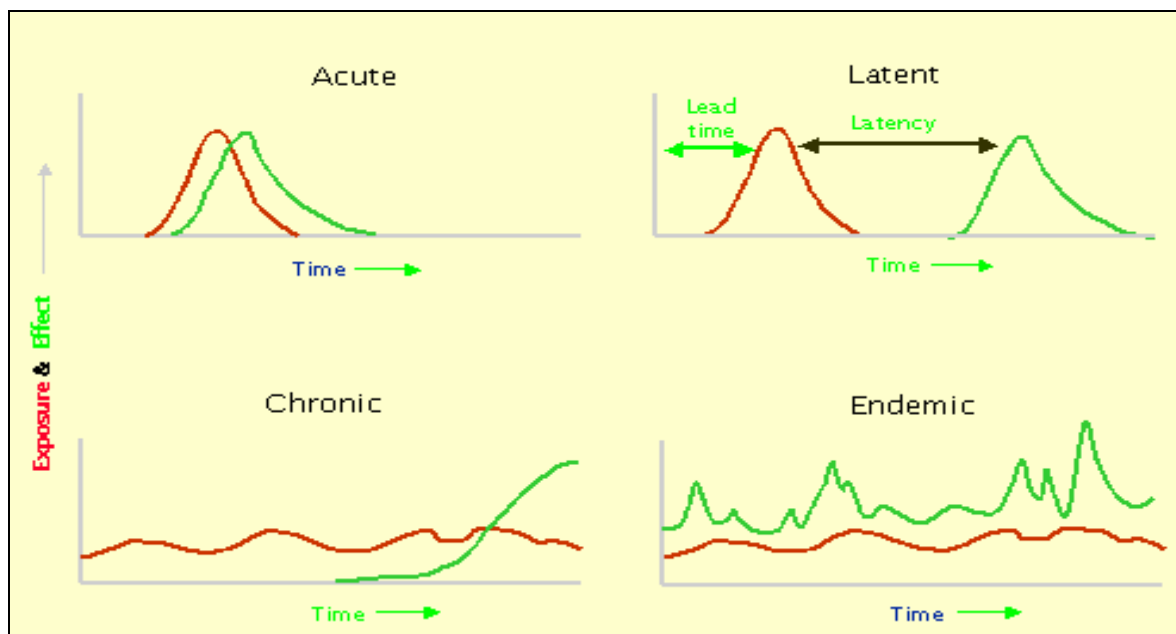


Figure 7. Temporal relationship of exposure versus health effects.

## 5.2. Modeling time-space exposures

In order to estimate exposure that takes place in time and space (Figure 8), specific models are used, which calculate the total exposure according to the equation below:

$$\text{Total exposure} = S (T_m * C_m)$$

where,

$T_m$  = time spent in micro-environment  $m$ .

$C_m$  = mean concentration in micro-environment  $m$ .

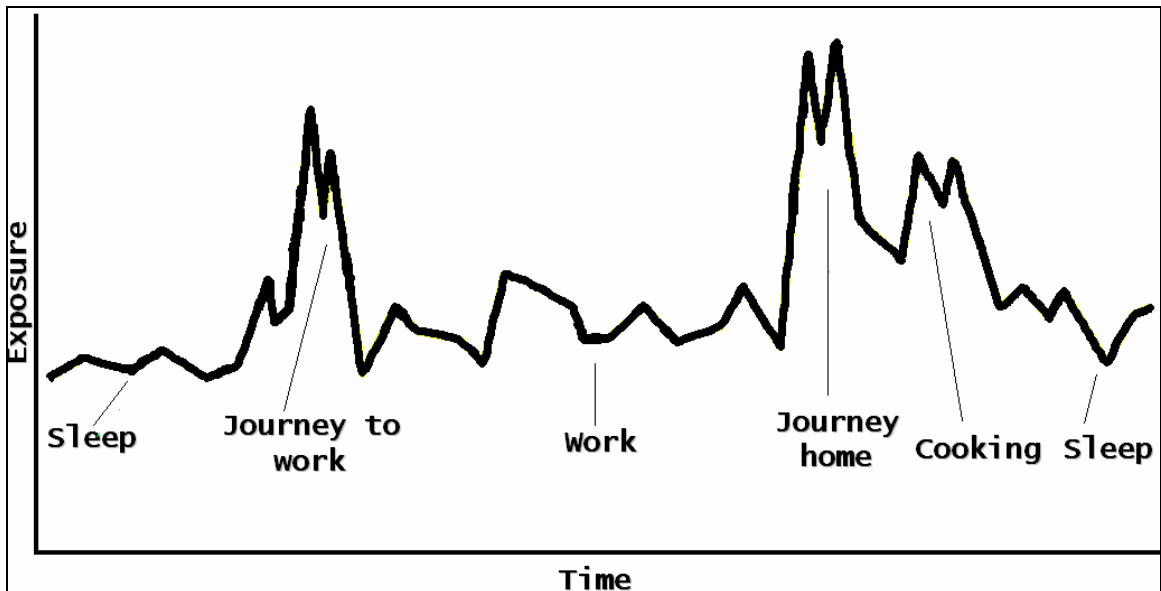


Figure 8. Exposure versus time and space.

In Figure 9, pathways of possible exposure by inhalation, dermal contact or ingestion of industrial/vehicle emissions, as well as, of other aqueous emissions are presented.

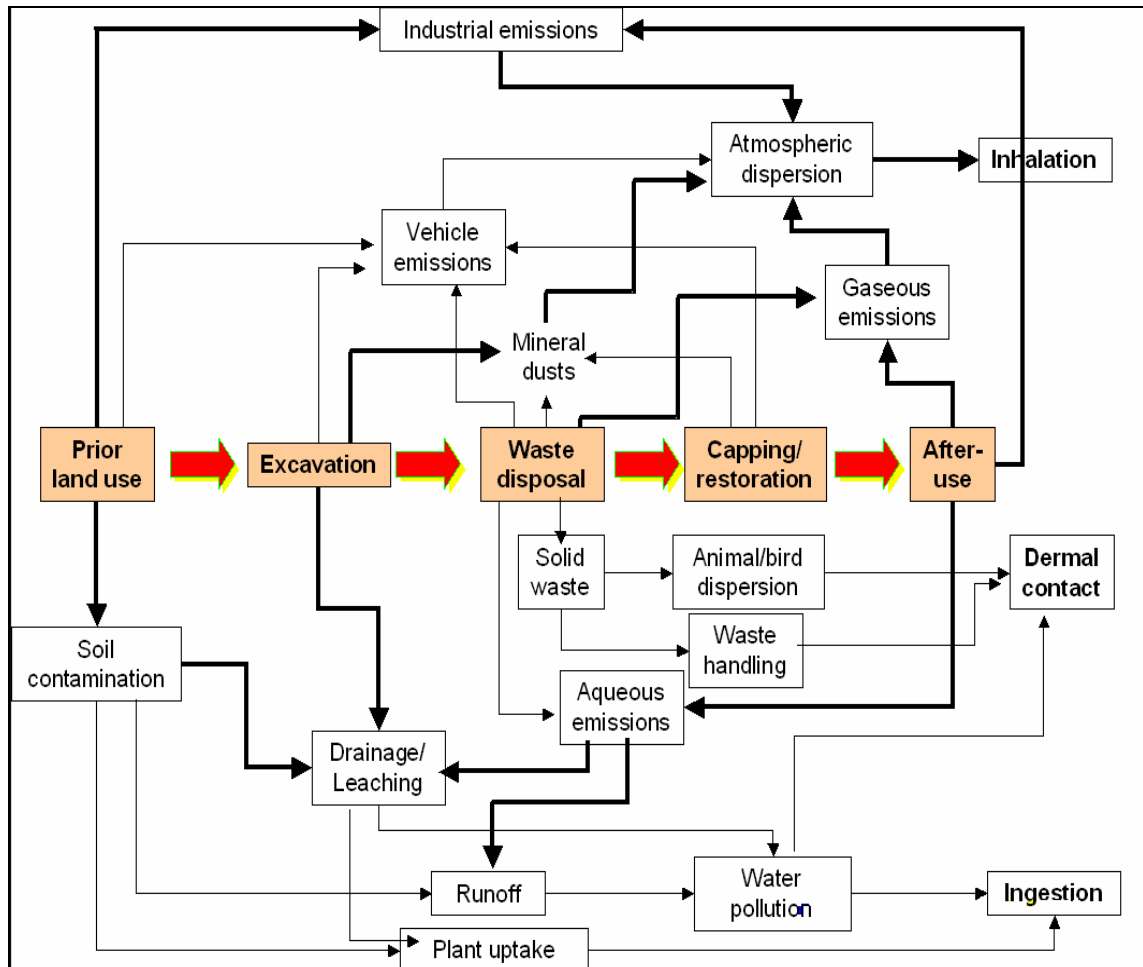


Figure 9. Pathways of exposure to air and water pollutants.

## 6.Environmental exposure assessment

In order to assess environmental exposure it should be taken into consideration that:

- Environmental concentrations and exposures are often low.
- Exposures often vary (geographically over short distances and temporally over short time scales).
- Exposure events are often brief and localised.
- Exposures may occur over a long time period (often long before any health effects are apparent).
- Health effects are small and confounded by other risk factors.
- Populations differ in terms of susceptibility and vulnerability (e.g. by age, gender, preparedness).

Thus, the possible research needs might be:

1. Large population-based studies to provide sufficient statistical data for health effects identification.



2. Exposure data, in order to cover large populations and sometimes long time periods, as well as, spatially and temporally highly resolved (individual or small-area scale) and short averaging periods.

In Table 8, methods for exposure measurement and modeling (occupational/environmental) are shown.

*Table 8. Methods for exposure measurement and modeling (occupational/environmental).*

<b>Type</b>	<b>Method</b>
Source activity	Production statistics
	Process modeling
	Distance from source
Emissions	Emissions monitoring
	Emissions modeling
Environmental concentration	Monitoring
	(Geo)statistical methods
	Dispersion modeling
Exposure/dose	Personal monitoring
	Exposure modeling
	Biomarkers (blood, urine)

However, there have been some studies regarding exposure assessment of particles. In Figure 10, the mortality rate versus the long-term particle pollution, especially the PM<sub>2.5</sub> and sulfate, are presented (D.W. Dockery et al., N. Engl. J. Med., 329 (1993) 1753). The concentrations are given in mg/m<sup>3</sup>. According to another study (EPA 1995) regarding the composition of fine particles PM<sub>2.5</sub> in Eastern U.S.A., it was found that about half of the PM<sub>2.5</sub> mass contained (NH<sub>4</sub>)<sub>2</sub> SO<sub>4</sub>.

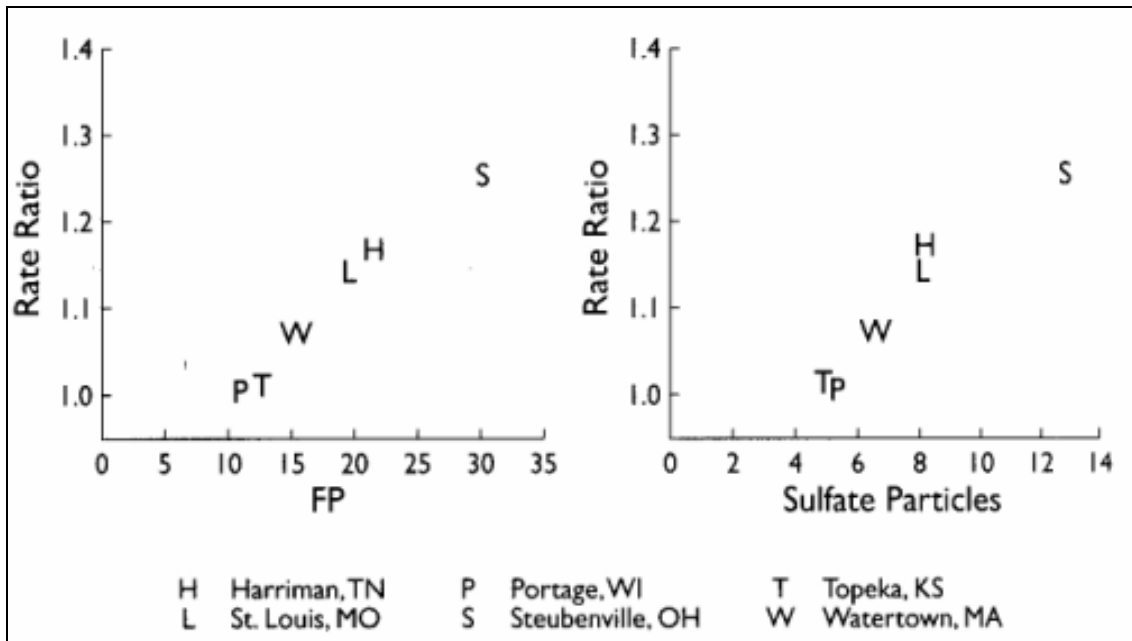


Figure 10. Mortality rate versus long-term particle pollution.

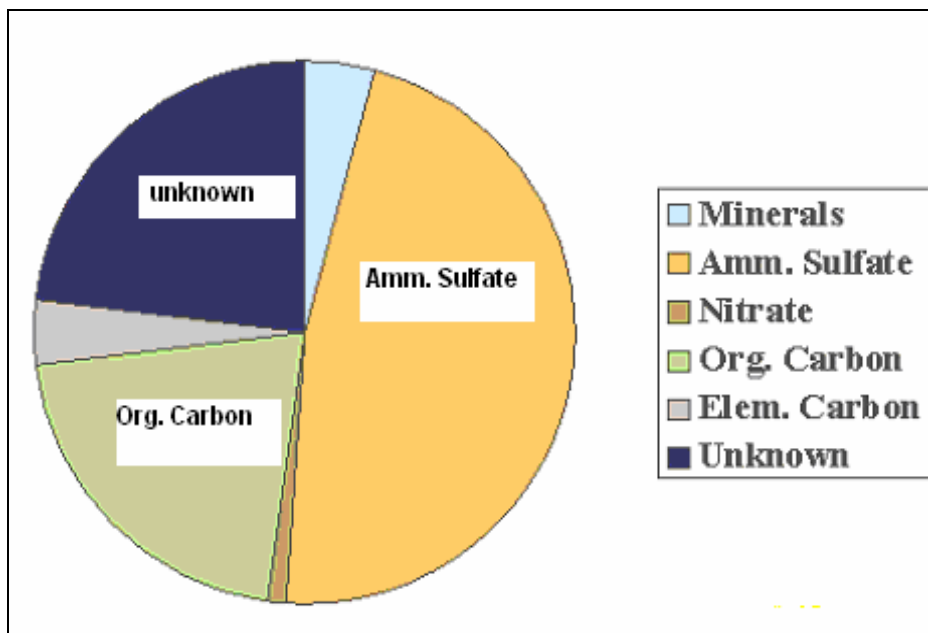


Figure 11. Composition of fine particles (PM<sub>2.5</sub>) in Eastern U.S. (EPA, 1995).

## 7. Emission sources of PM<sub>10</sub>

Particles, according to their emission source can be:

**1. Primary combustion particles**, (e.g. due to road traffic, power generation, industrial combustion processes). Generally, they are fine particles with diameter less than 2.5  $\mu\text{m}$  and often well below 1  $\mu\text{m}$ .

**2. Secondary particles**, which are formed in the atmosphere depending on their release in the gaseous phase, (e.g. sulphates and nitrates formed from emissions of SO<sub>2</sub> and NO<sub>x</sub>). Generally, they have diameter less than 2.5  $\mu\text{m}$ .

**3. “Coarse” particles**, can be originated from non-combustion sources, (e.g. re-suspended dust from road traffic, construction and mineral extraction processes, wind-blown dusts & soils, sea salt). Generally, they have diameter more than 2.5  $\mu\text{m}$ .

In Figure 12, some of the possible sources of ammonium sulfate and ammonium nitrate particles are presented. More specifically, ammonia can be released in the atmosphere from various sources, such as fertilizers, soil and vegetation, livestock, wild animals, which together with the SO<sub>x</sub> and NO<sub>x</sub> emissions from stationary, mobile or natural sources, react to formulate the respective particles.

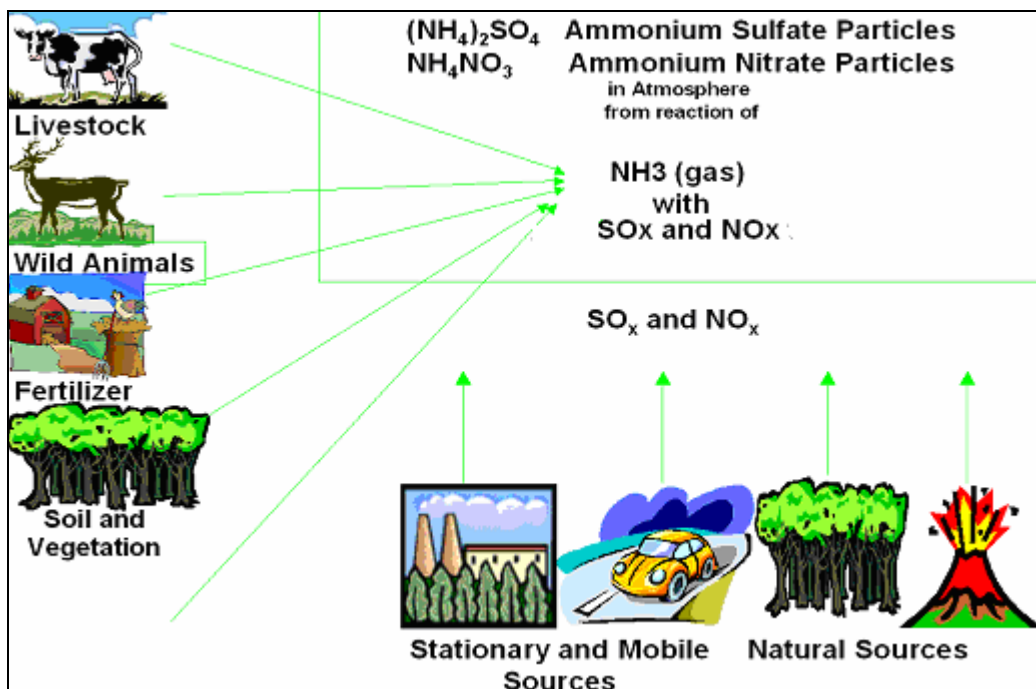


Figure 12. Possible sources of particles.

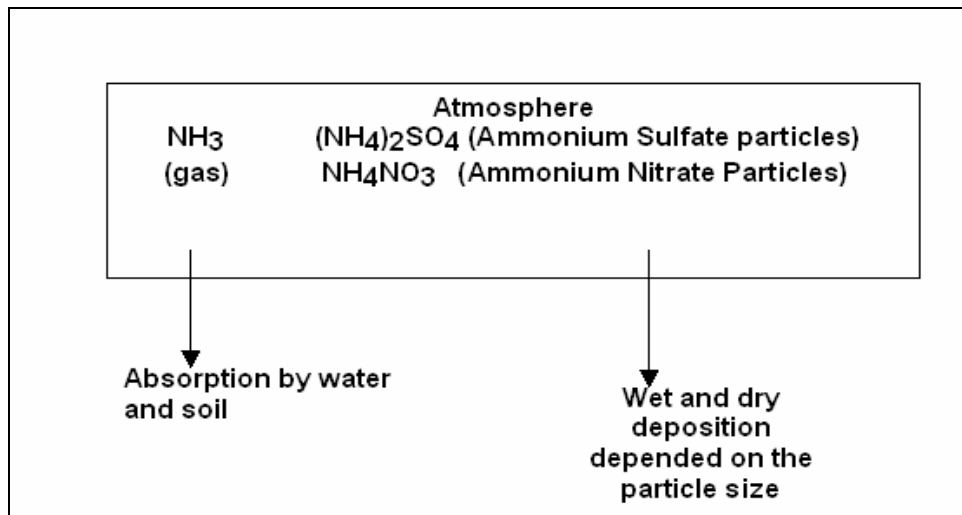


Figure 13. Air and soil pollution due to particles.

In Figure 13, it is shown that the residence time for ammonia and ammonium in the atmosphere is a few days and that there is a possibility to be absorbed by water and soil. The (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (ammonium sulfate) and NH<sub>4</sub>NO<sub>3</sub> (ammonium nitrate) particles can be deposited, depending on their size. According to a study, (J.B. Milford and C.I. Davidson, Journal of the Air Pollution Control Association, 37 (1987) 125), in airborne mass with diameter range from 0.5-1 μm, it was found that the most abundant ammonium compound in PM<sub>2.5</sub> is the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, as an average of 42 published distributions (Figure 14).

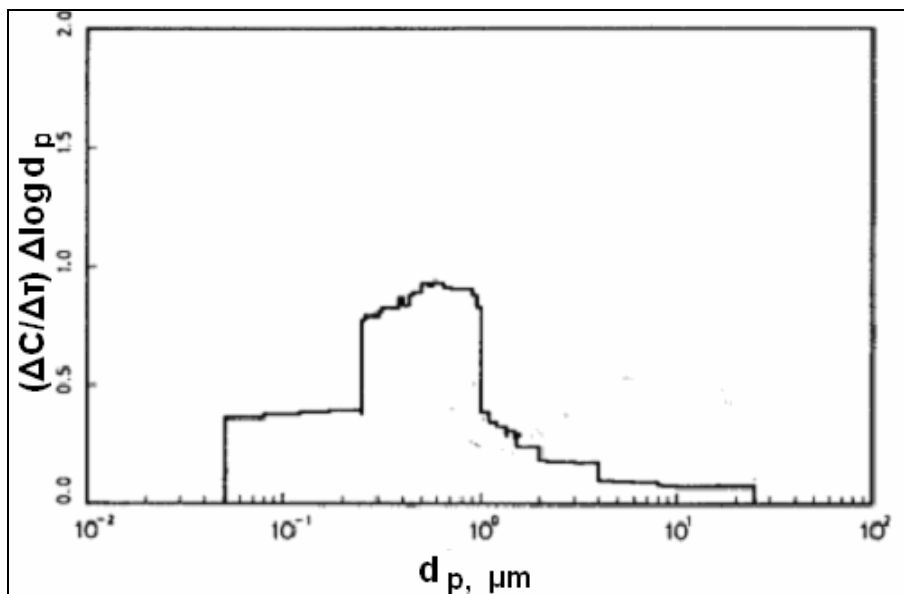


Figure 14. Size distribution of airborne sulfate mass concentration.

In Figure 15, the size distribution of airborne ammonium sulfate & nitrate mass concentrations in Claremont, CA (S.M. Wall et al., Atmos. Environ. 22 (1988) 1649), are shown. In Figure 16, total ammonia emissions by country for the U.S.A in 1995, are presented.

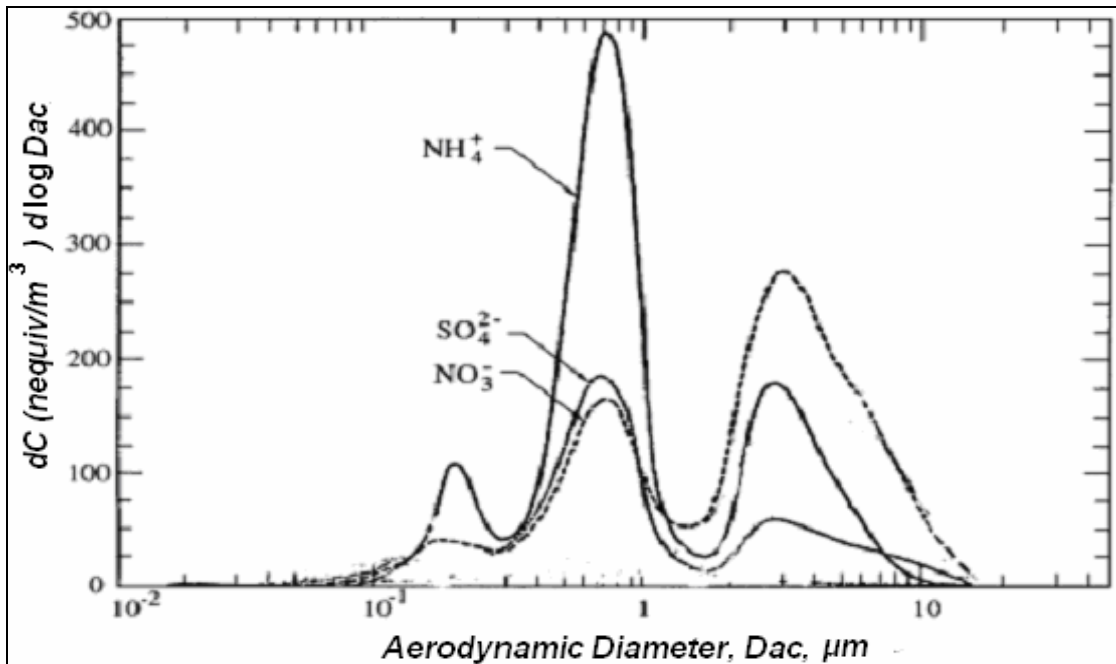


Figure 15. Size distribution of airborne ammonium, sulfate & nitrate mass concentrations in Claremont CA.

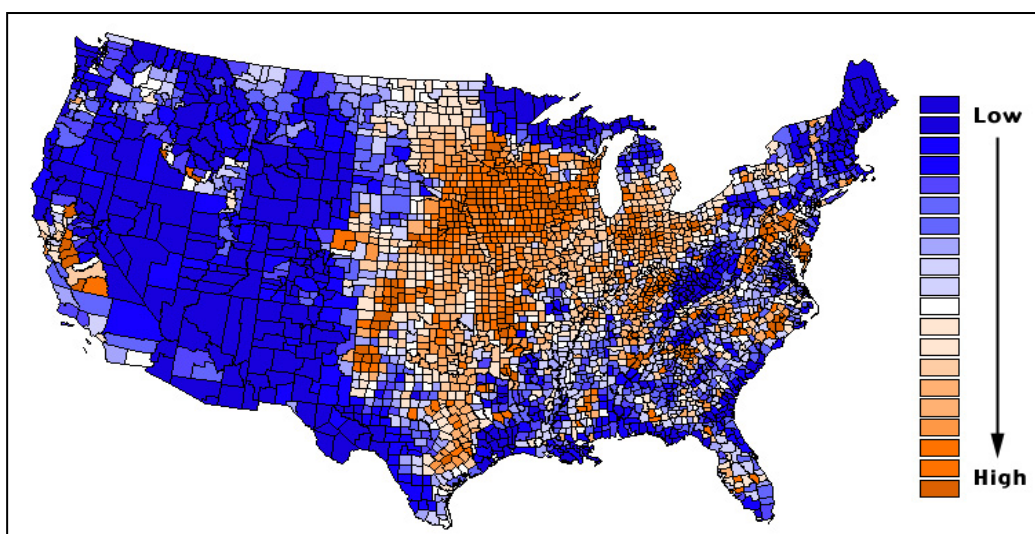


Figure 16. Total Ammonia emissions by Country, USA 1995.

## **8.Effects of PM**

### **8.1.Health effects**

Some of the important issues to investigate, in order to assess possible health effects of particles are:

- The inhalation of particles with diameter 0.5-1  $\mu\text{m}$  in pulmonary region and the possible resulted epidemiological data, such as correlation of death rate with  $\text{PM}_{2.5}$ .
- The asthma caused to children and how it is correlated with  $\text{PM}_{10}$ .

According to the WHO (Europe), 13.000 deaths of children have been reported the latest years in Europe with a rate of 0-4 deaths/y.

### **8.2.Other effects**

Another effect of particles is the impaired visibility. Visibility is most affected by particles with diameters similar to the wavelength of visible light, 0.4-0.7  $\mu\text{m}$ , such as  $(\text{NH}_4)_2\text{SO}_4$  particles. Particles can also damage the equipment and for that reason cleaning of room pollution is suggested.

## **9.International standards for particles**

### **9.1.The 1997 USA – EPA National Clean Air Act**

Every 5 years, a review of Health and Environmental (H&E) effects of  $\text{SO}_2$ ,  $\text{NO}_2$ , PM, CO & ozone in consultation with CASACommittee (Criteria Document & Staff Paper) takes place. Primary and secondary standards have been used to assess PM effects:

- Primary Standards, used for the assessment of the effects on public health.
- Secondary Standards, used for the assessment of the effects on public welfare and the environment.

$\text{PM}_{10}$ :  $50\mu\text{g}/\text{m}^3$  (annual),  $150\mu\text{g}/\text{m}^3$  (24-hour).

$\text{PM}_{2.5}$ :  $15\mu\text{g}/\text{m}^3$  (annual),  $65\mu\text{g}/\text{m}^3$  (24-hour).

## 9.2. Directive 1/1/2005: EU

According to the 1999/30/EC limit values for PM<sub>10</sub>, in an average meteorological year percentiles (P) are:

- P50: 67  $\mu\text{g}/\text{m}^3$  (winter 108  $\mu\text{g}/\text{m}^3$ )
- P98: 208  $\mu\text{g}/\text{m}^3$
- Annual: 33 to 50  $\mu\text{g}/\text{m}^3$
- Daily: 83 to 125  $\mu\text{g}/\text{m}^3$

According to this EU directive, a review regarding fine particles and their:

- health effects of size, number, composition,
- sources,
- chemistry & transport and
- measurement (technology –methodology),

took place in 2003. According to the WHO, no threshold is possible.

## 10. Occupational exposure limits (OELs)

Occupational exposure limits have been established by different health organizations. According to them, there are TLVs (Threshold Limit Values) & BEIs (Biological Exposure Indices), which can be:

- **Enforceable**
  - OSHA's Permissible Exposure Limits (PELs)(adapted TLVs).
  - 29 CFR 1910.1000, code for federal regulations.
- **Recommended (guidelines)**
  - ACGIH Threshold Limit Values (TLVs).
  - NIOSH Recommended Exposure Limits (REL).
  - AIHA Workplace Environmental Exposure Limits (WEELs).

### 10.1. Goals and limitations of OELs

The main goal of OELs is to protect the majority of the workers. Though, the main limitation are that:

- Hyper-susceptibility is not included. This can cause:
  - Discomfort.
  - Aggravation of pre-existing conditions.
  - Serious illness.
- A healthy worker is assumed.

- Out-of-work contributions assumed are negligible.
- A healthy lifestyle is assumed.

### **10.2.Threshold Limit Values (TLVs)**

Data provided from animal and human studies, industrial experience and expertise are updated periodically. These limits are designed to protect against a particular effect (critical effect):

- Impairment of health.
- Irritation.
- Narcosis, or nuisance.

### **10.3.Threshold Limit Values assumptions**

Threshold Limit Values assumptions take place by taking into consideration the parameters below:

- Young and healthy worker.
- 40 years of possible exposure.
- Model worker.
- Inhalation considered the main route of exposure.
- There is a “safe dose” for the listed chemicals (threshold chemicals).
- Exposure pattern: 8 hours/day & 5 days/week.

For unusual schedules, corrections according to the extension of the work-shift and the reduction of the recovery time have to take place.

### **10.4.Threshold Limit Value (TLV) concentration**

The unit used for gases and vapours is ppm (parts per million), defined as:  
1 ppm = one unit of volume of vapour contaminant per million units of volume of air (1  $\mu\text{L}$  in 1 L or 1 ml in  $\text{m}^3$  or 1 L in 1000  $\text{m}^3$ ).

The units used for gases, vapors and aerosols is the  $\mu\text{g}$  or mg of contaminant per cubic meter of clean air ( $\mu\text{g}/\text{m}^3$  or  $\text{mg}/\text{m}^3$ )



### 10.5. Threshold Limit Values (TLVs)

The limits used to assess exposure are the:

- Time-weighted average (TLV-TWA).
- Short-term exposure limit (STEL-TWA).
- Ceiling (TLV-C).
- Excursion limits.
- Skin notation.

More specifically, Time weighted average TLV (TWA-TLV) is the limit concentration for a normal 8-hour workday in a 40-hour workweek. In Figure 17, the time weighted exposure (TWA) and the TWA-TLV are shown.

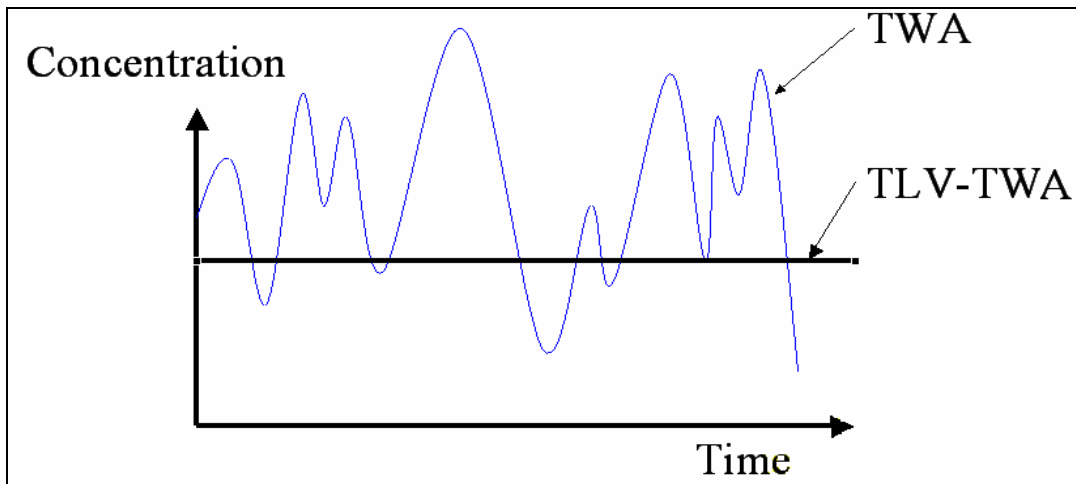


Figure 17. Time Weighted average exposure (TWA) and TWA-Threshold Limit Value (TLV).

Calculation of the TWA takes place by following the equations below:

$$TWA = \frac{C_1T_1 + C_2T_2 + \dots + C_nT_n}{T_1 + T_2 + \dots + T_n}$$

$$TWA = \frac{\sum_i C_i T_i}{\sum_i T_i}$$

It was decided to compare TWA with the published TLV-TWA:

- If the TWA < TLV-TWA it means underexposure, so it is accepted.
- If the TWA  $\geq$  TLV-TWA it means overexposure, so it is rejected.

### 10.6.Short Term Exposure Limit (STEL)

STEL is not a separate independent limit, but it supplements the TWA. More specifically, it is defined as the average concentration (TWA) to which workers can be exposed for up to 15 minutes, without suffering from:

- Irritation.
- Chronic or irreversible tissue damage.
- Narcosis of sufficient degree to create unsafe conditions.

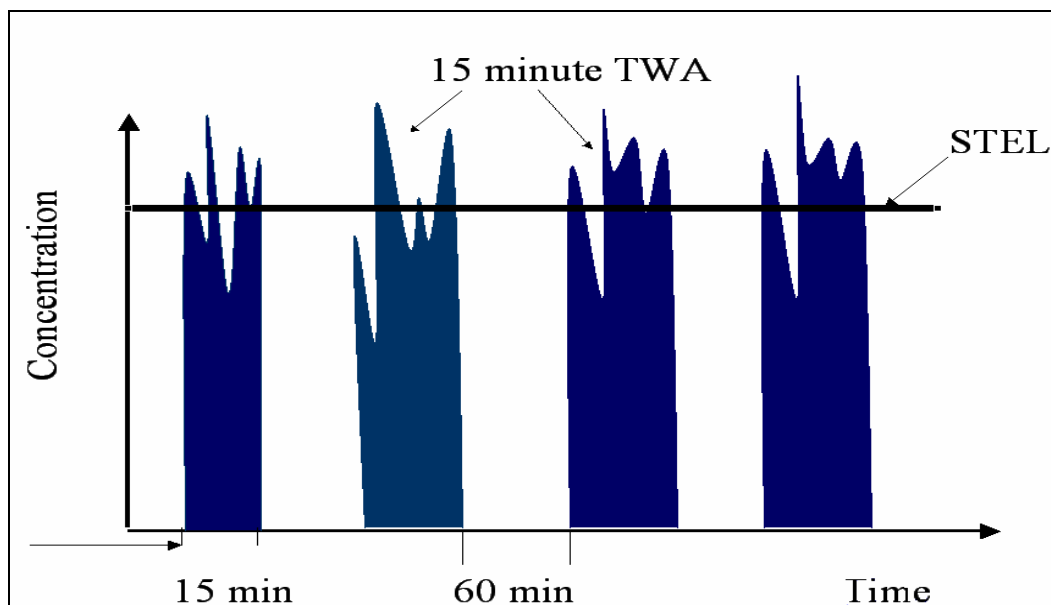


Figure 18. Short Term Exposure Limit (15-min TWA).

It was decided each (up to 4), of the 15-minute TWA ( $TWA_{15i}$ ) to be compared with the STEL-TWA value (Figure 18):

- If any of the  $TWA_{15i} > STEL-TWA$ , then there is non-compliance with STEL.
- If all of the  $TWA_{15i} < STEL-TWA$ , then there is compliance with STEL.

## 10.7. Excursion limits

Excursion limits:

- Are established for peak excursions (how high we want to accept peak values above the TLV-TWA).
- It is assumed that the TLV-TWA is not exceeded.
- No rigorous rationale is provided.
- Excursions may exceed 3 times the TLV-TWA for less than 30 minutes per day (not more than 5 times the TLV-TWA).

## 10.8. Ceiling (TLV-C)

Ceiling is the concentration that should not be exceeded during any part of the working exposure (Figure 19).

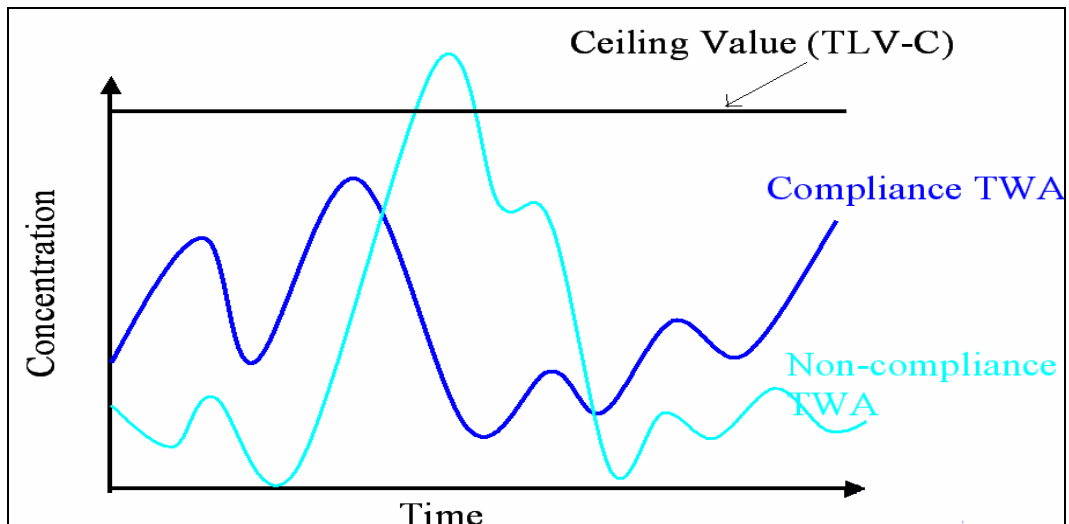


Figure 19. Ceiling Limit (TLV-C).

## 11. Exposure to mixtures

When the worker is exposed to a combination of different substances, then additive effect models for substances with same physiological effects are used, such as:

$$\text{total value} = \left( \frac{C_1}{TLV_1} + \frac{C_2}{TLV_2} + \dots + \frac{C_n}{TLV_n} \right) * 100$$

*total value < 100 : compliance*

*total value ≥ 100 : non – compliance*

Alternatively, independent TWAs for substances with different physiological effects are used.

## 12. Development of OELs

OELs have been developed taking into consideration:

- Identification of the effect to protect (critical effect).
- Routes of exposure.
  - Inhalation and skin.
- Physicochemical properties.
  - Vapor pressure, water/oil solubility, odor thresholds.
- Acute toxicity.
  - Lethal dose used to compare toxicity and for labeling requirements
  - Irritation studies (on eyes or skin).

For the development of OELs, sensitization studies are needed about:

- Determination of allergic reactions in animals.
- Metabolism and pharmacokinetics.
  - Studies on uptake, distribution, biotransformation, and excretion.
- Genotoxicity.
  - Use of bacteria, mammalian cells, insects.
  - Mutations to give indication of possible carcinogenic effects
- Reproductive / Developmental Toxicity.
  - Thalidomide example.
  - Teratology studies (on rats and rabbits).
- Neurotoxicity.
  - Behavioral guidelines by the EPA.
  - Irreversible effects.
  - Effect of learning and behavior on children.

## 13. Carcinogen classification by ACGIH

In below, classification of carcinogens according to the ACGIH is presented. The data have been confirmed either by human or animal studies.

- **A1: Confirmed human carcinogen**
  - Human data confirm (nickel subsulfide, bis(chloromethyl) ether, benzene, arsenic and chromium VI).

- **A2: Suspected human carcinogen**
  - Animal data and human data.
  - Human data conflicting.
- **A3: Animal carcinogen.**
- **A4: Not classifiable as a human carcinogen.**
- **A5: Not suspected as a human carcinogen.**

#### 14. Emissions from biomass burning

- *Fuel*: components of plant and litter – duff – humus (leaves and needles), cellulose (C<sub>6</sub> carbohydrate), hormones, oils and resins, terpenoids, pigments, steroids, metals.
- *Complete combustion products*: CO<sub>2</sub>, H<sub>2</sub>O, heat.
- *Incomplete combustion products*: a) trace gases: CO, CH<sub>4</sub>, hydrocarbons, NO<sub>x</sub>, NH<sub>3</sub>, HCN, organic N, b) VOCs (volatiles): aldehyde, acetone, methanol, vinyl acetate, c) particles: soot, minerals (prominent: potassium, sulfur, chlorine), organic mixtures (e.g. lignin pyrolysis products, anhydrous sugars, such as levoglucosan).

#### 15. PM measurements near fires

In below, data regarding PM values measured near fires are given:

- In the wildfires of Polhenus (2001), Schonover (2002) and Snaking (2002), the indoor levels of PM<sub>2.5</sub> increased about 57-100% compared to the outdoor concentrations, when the windows were closed; the air cleaners reduced indoor PM<sub>2.5</sub> by an average of 80%; indoor & outdoor background PM<sub>2.5</sub> were at a similar level of 3-5 μg/m<sup>3</sup> (Miller and Hannigan, 2002, <http://spot.colorado.edu/~hannigan/envimpact.ppt>).
- In Hoopa Valley, CA (1999) wildfires, PM<sub>10</sub> were more than 350 μg/m<sup>3</sup> for over a week and more than 425 μg/m<sup>3</sup> for two days (J.A. Mott et al., Western J Med 176 (2002) 157).
- In Indonesian forest fires (1997), particles were up to 15 times compared to the 260 μg/m<sup>3</sup> limit for about 2 months (WHO, 1999).
- In Hamilton MT (2000) wildfires, PM<sub>10</sub> reached more than 999 μg/m<sup>3</sup> for 1-hour and were at the range of 300-600 μg/m<sup>3</sup> for many days (S. Miller and M. Hannigan, 2002, <http://spot.colorado.edu/~hannigan/envimpact.ppt>).

➤ **Air-quality and personal protective equipment in operational procedures**  
(N. Raffalli, CEREN, Fr)

## 1. Introduction

*“Today, it is no longer «save or die», but better save in order to not die”.*

Colonel Bardo

Many fire-fighter accidents have been reported due to cardio-vascular symptoms, intoxication from CO or headache. The question raised is: does this happen due to a toxic environment? These studies were initiated in 1995 by CEREN and the Colonel PRIM, chief doctor of the Var fire-fighters (department in the South of France). A number of experiments took place in the laboratory, in prescribed burnings and in real forest fire incidents. The results, regarding the smoke chemical composition, as well as, information about the personal protective equipment of a fire-fighter will be presented.

## 2. Fire experiments and equipment used

### 2.1. Fire experiments carried out:

- In the laboratory.
- During prescribed burnings.
- During real fire occurrences.

In order to obtain comparable results, it is necessary to specify a common procedure for each experiment (Figure 1).

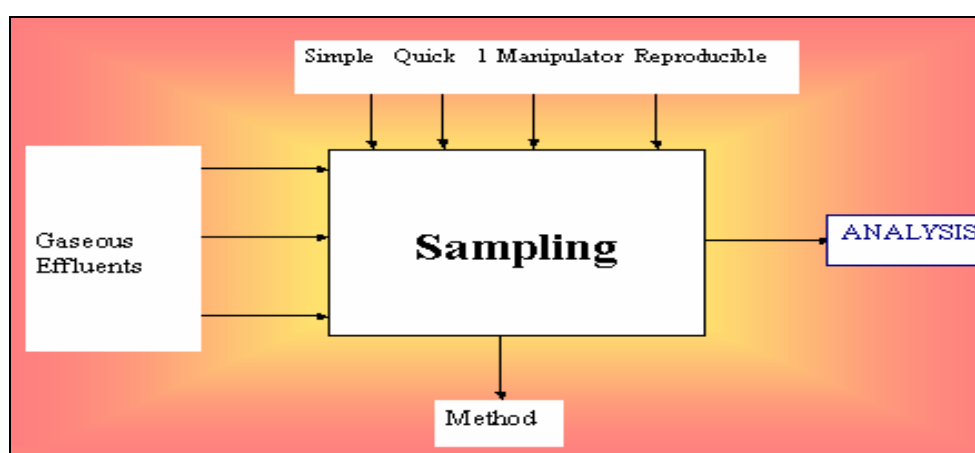


Figure 1. Schematic diagram of the analysis method.

## 2.2.Presentation of the equipment used

The equipment used for the analysis was:

- A Thermal Desorber type device (ATD) and a Mass Spectrometer, coupled with a Chromatographer in gaseous phase (ATD-GC-MS analysis), as shown in Figure 2. In Figure 3, a typical chromatogram resulted from the ADT-GC-MS smoke analysis is presented.



Figure 2. Thermal desorber, Gaseous phase Chromatographer and Mass Spectrometer Turbo Mass Gold (Perkin Elmer).

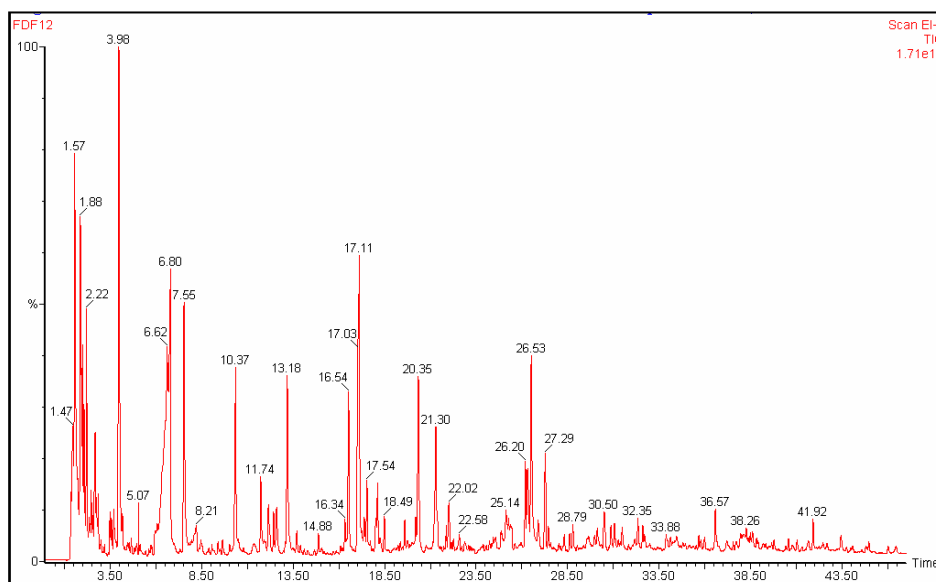


Figure 3. Chromatogram resulted from smoke samples analysis by using the ATD GC-MS system.

### 3. Analysis assessment

- Samplings were carried out during:
  - Epiradiator burnings.
  - Tests in the Fire Tunnel (Figure 4).
  - Prescribed burnings.
  - Real fires (Figure 5).
- Only the molecules having a molar mass over 60 g/mol were analyzed by the ATD-GC-MS method. Furthermore, many particles are produced during fires according to studies that have been carried out by different European laboratories (Greece, Portugal).



*Figure 4. Smoke sampling in fire tunnels and in the laboratory.*





Figure 5. Smoke sampling during real forest fires.

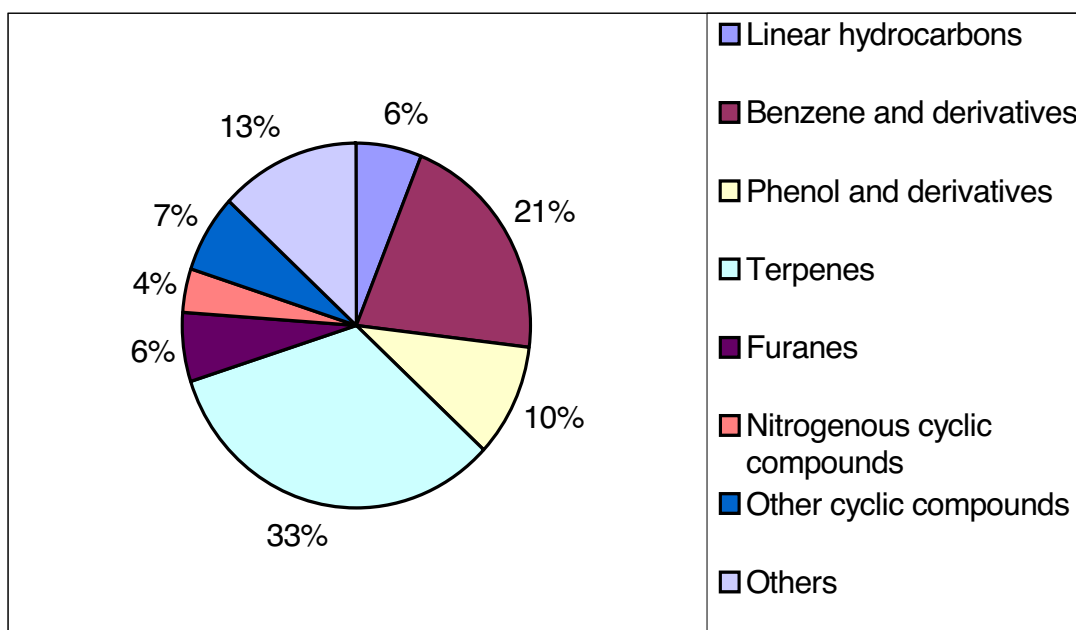
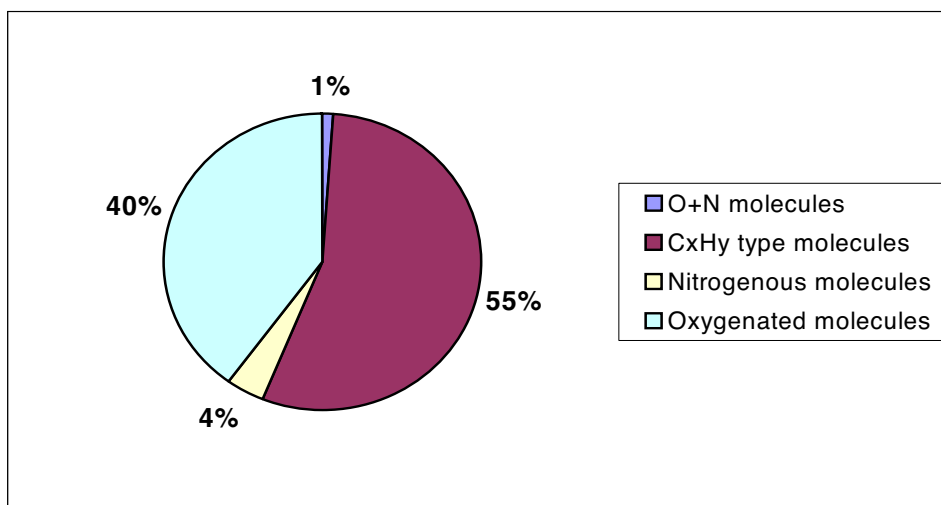


Figure 6. Composition of the smoke samples analyzed.



*Figure 7. Smoke composition according to component type.*

According to Figure 6, the 33 % of the smoke components in the smoke samples analyzed is attributed to terpenes, the 21% to benzene and derivatives, the 10% to phenols and derivatives, the 6% to linear hydrocarbons and the other percents to 6% furans, 4% nitrogenous cyclic compounds, 7% other cyclic compounds and 13 % others.

According to Figure 7, the 55 % of the molecules is attributed to hydrocarbons, the 40 % to oxygenated molecules, the 4% to nitrogenous molecules and the 1% to molecules consisting of oxygen and nitrogen.

#### **4. Personal protection equipment**

In Figure 8, the personal protective equipment of a fire-fighter is shown and in Table 1, the National and European standards for protection equipment are presented.

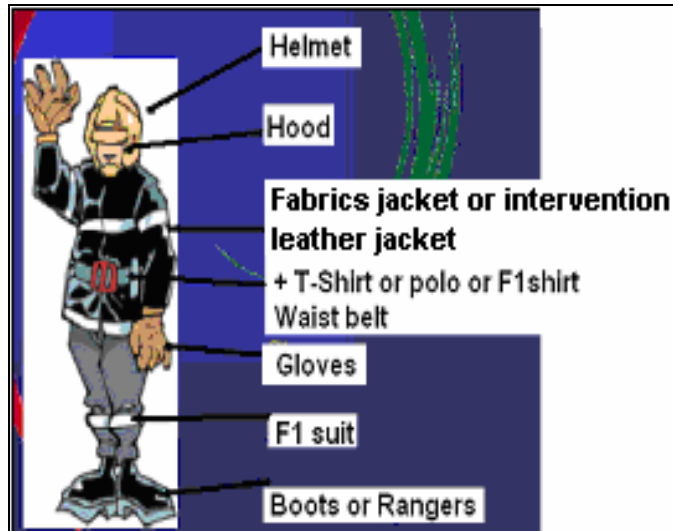


Figure 8. Personal Protection equipment of a fire-fighter.

Table 1. National and European standards for personal protection equipment.

Elements	National Standards	European Standards
<b>F2 Helmet</b>	NIT 312	EN 443
<b>Hood</b>	NIT 328	EN12911
<b>Fabrics intervention jacket or</b>	NIT 324	EN469
<b>Leather intervention jacket</b>	NIT 327	EN469
<b>Gloves</b>	NIT 306	EN659
<b>F1 suit</b>	NIT 301 NIT 302 NIT 303	EN531
<b>Polo</b>	NIT 316	
<b>F1 shirt</b>	NIT 313	
<b>T shirt</b>	NIT314	
<b>Shoes (rangers or boots)</b>	NIT 308 NIT 309 NIT 310	EN345
<b>Waist belts</b>	NIT 326	EN358



*Figure 9. Head and facial protection equipment.*

#### **4.1. Escape mask**

The escape mask (Figure 10):

- is used only in the South of France (department Bouches du Rhone).
- has no « legal » obligation.
- is used to reach a survival area, must not be used during the fight.



*Figure 10. Escape mask.*

## **5. Conclusions and perspectives:**

- Many studies have described the quality of the air surrounding fire-fighters, but what about its impact?
- Furthermore, as fire-fighting is a physical activity, what type of breathing protections can be used by fire-fighters?
- Finally, due to the urbanization of forest areas, we have a new problem: how can we protect this population from intoxication risks?

### **➤ Effects of forest fire smoke**

***(G. Cesti, Regione Valle D' Aosta, Responsabile di Servizio del Fuoco della Foresta, It)***

#### **1. Introduction**

Forest fires and the smoke produced can have various negative effects on the population and the environment. In this presentation, possible forest fire smoke effects are discussed. Information on the chemical composition and formation of smoke, as well as, toxicology issues regarding some forest fire smoke components, such as CO, particles, aromatic hydrocarbons, etc, are presented. Protection of the fire-fighters, by using protective means for eyes and respiratory system, is discussed.

#### **2. The study of smoke**

- The study of forest fire smoke effects is relatively recent.
- The first specific studies (U.S.A) took place at the end of 1980 (fires of the Park of Yellowstone and Rocky Mountains).
- Although a number of preliminary results on that issue exist, there is a need for further research.

##### **2.1. Variation in the chemical composition of smoke**

Various types of combustibles and conditions of combustion determine different chemical composition of smoke, in forest or building fires.



*Figure 1. Fire in a building.*

Possible components in forest fire smoke can be carbon dioxide, carbon monoxide, not burned particles, aldehydes and phenols, aromatic hydrocarbons, ozone and free radicals. In comparison, the smoke produced by industrial or building fires is chemically very complex too. However, possible components in the smoke of industrial fires can be the same as those of forest fires and in some cases can contain: hydrocyanic acid, hydrochloric acid, phosgene, ammonia, sulphur dioxide, peroxidize of nitrogen etc.

## **2.2. Conditions of combustions and smoke formation**

The conditions of combustion affect the smoke formation. More specifically, flames without significant smoke can be observed in complete combustion, whereas sharp flame and smoke can be seen in incomplete combustion and very intense smoke, with no flames, in latent combustion.

- *Almost complete combustion*, where mainly  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are involved.



*Figure 2. Visible absence of smoke in almost complete combustion.*

- *Incomplete combustion*



*Figure 3. Rapid and intense incomplete combustion, when significant quantities of forest fuel are burned.*

- *Latent combustion*



Figure 4. Smoke generated by smouldering fire, rich in CO.

- *Specific conditions*

If smoke rises at the time of anti-cyclonic conditions, then there are no significant smoke problems (Figure 5).



*Figure 5. Smoke in anti-cyclonic conditions and smoke laminated, moving slowly in dispersing.*

The conditions of temperature inversion can cause persistence of smoke for several days.



*Figure 6. Smog remaining in the environment, due to specific temperature conditions.*

### **3. Smoke detection positive effects**

Smoke detection can give indicative information regarding:

1. The localization of fire incident (Figure 7).
2. Type of forest fuel burned (Figure 8).
3. Type of the fire.
4. Direction of the wind, turbulences.
5. Secondary fire-spots.





*Figure 7. Localisation of fire incident.*



*Figure 8. Type of forest fuel burned.*

#### **4.Negative effects of smoke**

- Reduction of the visibility and feeling confusion.
- Reduction of the visibility, obstructing the movement of the helicopters or the airplanes but also of the ground vehicles (Figures 9,10).
- Toxic effects in the short and long term for the personnel engaged in the fight.
- Toxic effects for the population.
- Air pollution.



*Figure 9. Reduced visibility for the aerial means.*



*Figure 10. Reduced visibility for the ground means, danger on the roads.*

## 5.The triangle of the risks



## 6.Toxic effects of smoke

### 6.1.CO<sub>2</sub>

Carbon dioxide is produced in significant quantities in a forest fire. Although it does not have direct toxic effects, it causes an increase of the respiratory frequency and in that way it contributes to increased quantities of inhaled smoke pollutants (gases and particles). More specifically, a CO<sub>2</sub> concentration of 3% can cause a doubling of the respiratory frequency.

### 6.2.CO

Carbon monoxide is also produced in significant quantities in a forest fire, either in the phase of sharp flame or in the smouldering phase. It is a very toxic gas and in high concentration (greater than 1,3%) can cause even death. The effects are caused due to high concentrations of CO. More specifically, 10 min of activity in the presence of such concentrations can cause disorders.

Carbon monoxide is colourless and odourless gas, which binds very quickly to haemoglobin of blood to form carboxyhaemoglobin. In Table 1, the % concentration of COHb in blood and possible health effects are presented.

Table 1. The % concentration of COHb in blood and possible health effects.

Carboxyhaemoglobin (COHb)%	Effects
< 1	No specific sign of intoxication
1 - 2	Problems of behaviour at the subject
2 - 5	Movement and eye troubles
5 - 10	Cardiovascular and respiratory disorders
10 - 20	Aggravation of the preceding symptoms and appearance of cephalgia, nausea, somnolence and vomiting
20 - 80	In progression: strong cephalgia, nausea, vomiting, giddiness, tiredness, cardiovascular collapse, coma, convulsions, turbid respiratory serious, dead

After 3-4 hours of exposure of a fire-fighter to a CO concentration of 35 ppm, possible symptoms can be tiredness and confusion. The duration of exposure to smoke is very critical, so as to estimate the concentration of COHb in blood. In Figure 11, COHb% concentration in blood is plotted versus the exposure duration (h) to 50, 100 and 200 ppm of CO.

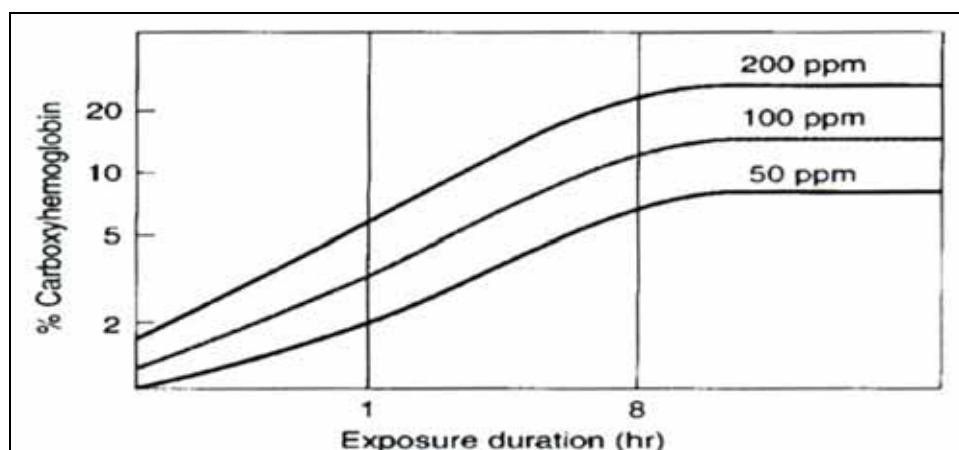


Figure 11. Exposure duration to 50, 100 and 200 ppm of CO and correlation to COHb%.

### **6.3. Particles**

Particles are produced in significant quantities during combustion. According to their dimension they are classified as: 1) coarse particles, with larger average diameter of 10  $\mu\text{m}$  and 2) fine particles, with average diameter in the range of 0,3  $\mu\text{m}$ . Smouldering fires generate a greater quantity of fine particles, in contrary to the combustion with flames, where significant quantities of coarse particles are released. Coarse particles are stopped by the cells of the respiratory tracts, whereas fine particles can penetrate the lungs. Carcinogenic compounds can be absorbed by the fine particles and in that way can penetrate the air cells. The toxic effects of particles are little known from an epidemiologic point of view.

### **6.4. Aldehydes and phenols**

Aldehydes (acrolein and formaldehyde in particular) are considered irritants and are formed under conditions of incomplete combustion. Phenols (phenol, cresol, etc) are also produced under conditions of partial combustion of forest fuels, though their concentrations are low. Aldehydes and phenols are strongly irritating for the human mucous membranes. Formaldehyde is also potentially carcinogenic. Irritation of the first respiratory tracts is caused by acrolein and formaldehyde. A long exposure to those compounds also increases the sensitivity to the respiratory affections. Concentrations greater than 10 ppm can be mortal.

### **6.5. Aromatic hydrocarbons**

Aromatic hydrocarbons can be released in the atmosphere or can be condensed on particles, either absorbed by them. They are considered carcinogenic, (e.g. benzo-anthracene, benzopyrene). However, it seems that the epidemiologic risk for the fire-fighters due to aromatic hydrocarbons is not significant.

### **6.6. Ozone**

Ozone is formed by photochemical effect of the solar radiation. A certain concentration can be found close to the ground in fires at high altitude. It is strongly oxidizing and for that reason it is harmful for human tissues. However, its low concentration at the time of a forest fire leads to unimportant toxic effect.

## 6.7.Free radicals

Free radicals are compounds, which are produced during the combustion, before their recombining in new chemical compounds. Although they have short half-life in general, some radicals can survive up to 20 min. The toxic effects of the free radicals are not known, but due to the short duration of their life it can be concluded that the toxic effect because of the exposure to those compounds is not very significant.

## 7.The risk of dense smoke (smoky conditions)

During exposure and inhalation of dense smoke, e.g. when a fire-fighter is performing his duties on the head of a fire, signs of asphyxiation can be observed. This symptom is related to the toxicity of smoke. In general, this does not affect the population in general, but people with respiratory or cardiac problems might be at risk.

## 8.Protection of the fire-fighters

### 8.1.Factors which affect the risk of exposure to smoke

- 1.Physical predisposition of the fire-fighter.
- 2.Chemical composition of smoke.
- 3.Location of the fire-fighter (site).
- 4.Duration of the work in the position considered.

### 8.2.Types of protection

**Preventive protection:** medical examination (initial and periodically repeated)  
The risks of smoke can be important for the subjects with cardiac and respiratory problems or other pathologies, which are in correlation with cardiopathies and respiratory disorders, as well as for smokers. It is necessary to recognize those data at the time of the initial medical visit.

**Active protection:** application of a tactic of correct attack. In Figure 12, active protection of fire-fighters in regard with the position that they must have in the fire are shown.

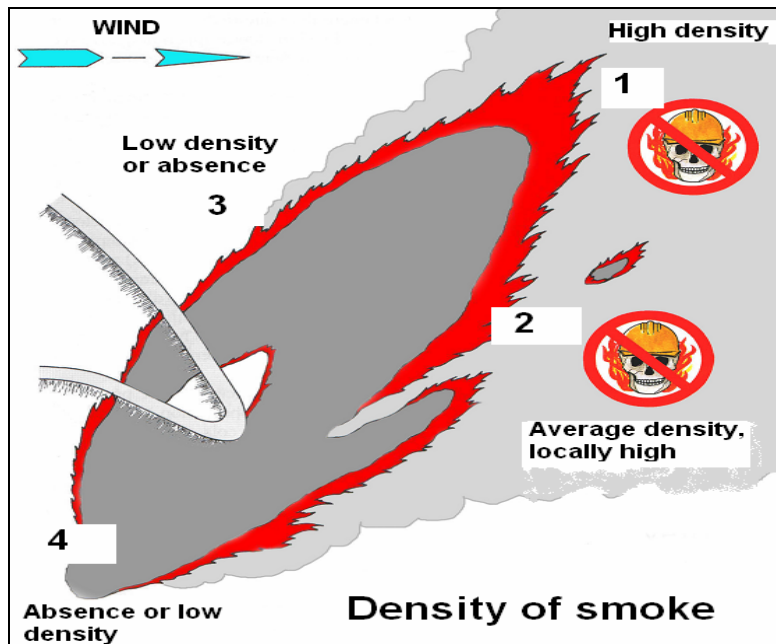


Figure 12. Active protection - positions compared to the fire.

Site 1: Head of the fire. Not possible to remain for a long time on the head. Continuous exposure to dense smoke takes place.

Site 2: "Hot" side under the wind. Dense smoke exists. Difficulty in remaining for long time on the side is encountered. Continuous exposure to dense smoke takes place.

Site 3: "Cold" side under the wind. Smoke of low density exists. There is a possibility of working a long time on the side. Exposure to negligible smoke (depending on the direction of the wind) takes place.

Site 4: Tail of fire. The smoke is absent or of low density. There is a possibility of working a long time on the tail. Exposure to negligible smoke takes place.



Figure 13. Position upstream of the fire.

**Passive protection:** application of glasses, masks or other specific systems. These systems must protect the eyes and the nose, as well as, the mouth, must answer ergonomic criteria, should be put quickly in correct way, should not be heavy and cumbersome.

The critical question is: When are these systems used? One must be able to work with the systems or one uses them only in difficult situations?

### 8.3. Protection of eyes

The protection of eyes ensured by special glasses, with the characteristics below:

1. Good side vision.
2. Demister.
3. Good adherence with the face.
4. Compatible with the helmet and the hood.
5. Fireproof.

### 8.4. Protection of respiratory system

In theory, it is not possible to use insulating breathing apparatuses because they are too heavy and cumbersome. Moreover, toxicity of smoke, as well as, time of exposure may not justify their use.

Protection of respiratory system can be ensured by using special masks with the following characteristics:

1. Sufficient filtration of the particles (at least particles with diameter of  $10\ \mu\text{m}$ . A more reduced diameter would be desirable, such as  $0.3\ \mu\text{m}$ , but increases also the resistance of the air flow).
2. Good adherence with the face.
3. Compatible with the helmet and the hood.
4. Fire-proof.

### 8.5. Tactics of attack

During the attack, fire-fighters are at risk, because they are exposed to a very dense smoke, especially when they are performing their duties near the head of the fire (Figures 14, 15).

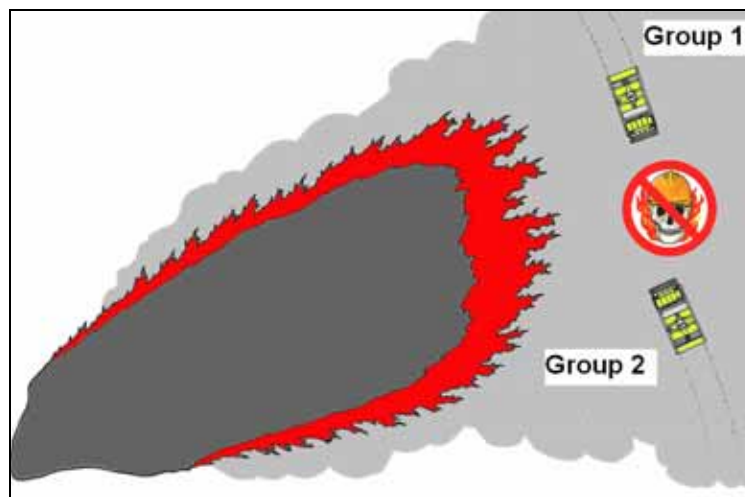


Figure 14. Tactics of attack (groups near the head of the fire).



Figure 15. Smoke on the head of the fire.



The attack on the sides of the fire exposes less fire-fighters to smoke (Figure 16).

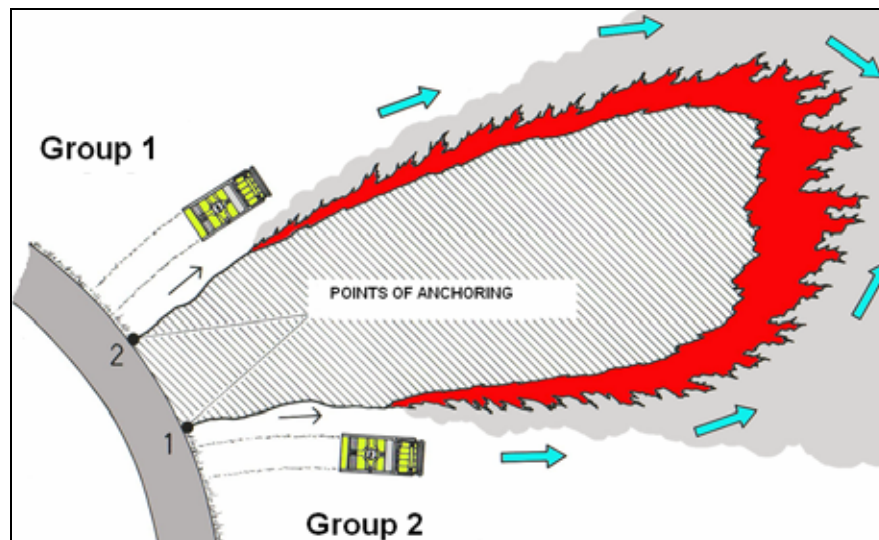


Figure 16. Attack on the sides of the fire.

## 9. Phases of the extinction

### 9.1. Control of the flames

The duration of this phase varies, depending on the specific case. For example, it lasts longer in case of attacks that the fire-fighters are very close to the flame-front and the smoke. The duration decreases with the use of water, although this can result to the increase of smoke quantity produced. It is proposed to change shifts frequently.

### 9.2. Security of the perimeter

Duration of this phase also varies, but usually it is longer compared to the phase of the control of the flames. More specifically:

- The quantity of smoke decreases gradually during this phase.
- The exposure to smoke is of longer duration, despite the use of water.
- The quantity of smoke is not very important, but there is the danger of carbon monoxide.

The change of shifts has fixed periods.

### **9.3. Monitoring**

Although the duration of this phase is long, the exposure of the fire-fighters is not considered very significant because the quantities of smoke are reduced and dispersed. Change of personnel takes place under specific conditions.

### **10. Exposure time to smoke**

Depending on the dimensions of the fire, the exposure time to smoke is affected. More specifically:

**Small fire:** exposure time between 1-2 h.

**Average fire (2-3 ha):** exposure time between 3-5 h (1-2 h for the control of the flames and 3-4 h for the final extinction).

**Large fire:** duration without significance, one must speak about work period of each fire-fighter.

## ***Session 3: Other issues***

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This session includes presentations referred to various ffs issues, such as complexity of forest fire smoke (ffs) and also application of a risk assessment method on ffs, in order to assess ffs possible adverse effects on receptors. The presentation that follows proposes a method for the development and validation of forest fire models and shows that, in special cases, ffs can contain radioactively contaminants.

➤ **Using of a radioactive marker for verification of dynamic models of forest fires at an experimental site located in the Chernobyl Exclusion Zone**  
*(V. Poyarkov, European Center of Technological Safety, Kiev, UKR)*

### **1. Introduction**

One of the significant components of hazard, attributed to forest fires, is the release of toxic materials from forest contamination, as a result of burning. Existing dynamic models, describing a release and dispersion of toxic materials during a forest fire, are based on mathematical modeling of burning processes, release and dispersion. However, for their verification, it is necessary to have detailed experimental data, which could be obtained only as a result of accomplishment of a site experiment. This can be achieved by using a tracer as a radioactive marker. The present work is attributed to the way that a radioactive marker could be used for verification of dynamic models of forest fires at experimental site, which is located in the Chernobyl (ChNPP) Exclusion Zone.

### **2. Tracer as a key for input data and model verification**

A basic requirement for accomplishment of dynamic models of release and dispersion is availability of a marker (a tracer), which would enable to obtain quantitative characteristics of a release and dispersion of toxic materials. A tracer content in burning products would enable to determine experimentally a height of elevation and dispersion composition of gases and particles, their distribution in different air levels, concentration at different distance and altitude from a fire site, etc.

It is suggested to use as markers radionuclides that have entered into forest ecosystems, as a result of the Chernobyl NPP accident (V. Poyarkov et al., *The Chernobyl Accident. Comprehensive Risk Assessment*; English Edited by G. Vargo; Battelle Press, Richland, USA, ISBN 1-57477-082-9, 2000).

High concentration of radionuclides in forest fuels and relatively simple determination of their concentration enables to obtain reliable experimental data for quantitative assessment of fire parameters. It is suggested to ignite a prescribed forest fire on a forest site within the Exclusion Zone.

### 3.Site for the Exercise

A nowadays territory of the ChNPP Exclusion Zone and the whole locality along the coasts of the rivers of Pripyat' and Uzh were completely covered by forests. The fire was natural satellite of pine tree forests, dominating on that territory, providing pyrogenic cycles of natural renovation of tree-stands. The forest fires are usual phenomenon on the territory of the nowadays Exclusion Zone.

Considerable stocks of pine tree forest litter are a basic condition for initiating large wildfires. Land of young pine tree cultures and pine tree cultures with age between 20-40 are prevail in the Exclusion Zone; that is why the probability of forest fires in general is significantly higher than in natural forests and especially crown fires.

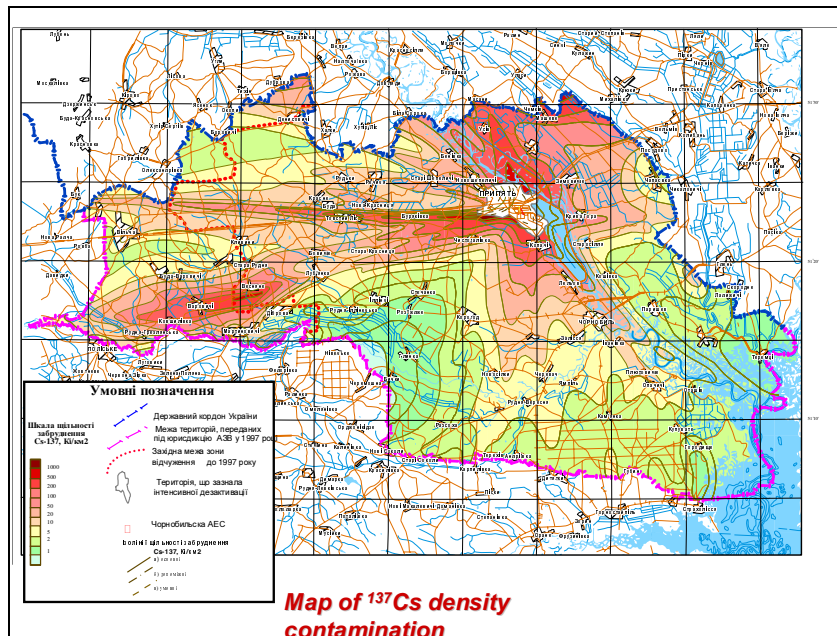


Figure 1. Chernobyl area  $^{137}\text{Cs}$  contamination.

Now the number of ignitions in forests and at abandoned agricultural land, reaches in average about one hundred cases per year. The 95% of them appear during the fire-dangerous period.

#### **4.Goals and objectives**

The proposing experiment has goal:

1. To obtain input data for verification of models describing a release and dispersion of toxic materials during the forest fire.
2. Based on experimental data, to verify existing models of elevation and dispersion of aerosols and other burning products.
3. To evaluate forest fire impact on transfer of radionuclides and other toxic substances.
4. To accomplish testing of new technologies on forest fire extinguishing and stabilisation of a post-fire situation.

The work foresees the following tasks:

- Determination of distribution characteristics of radionuclides stock (a tracer) generally in the ecosystem and in the types of forest fuels during a pre-fire period.
- On-line instrumental monitoring of the flame-front parameters, such as temperature of separate types of forest fuels burning.
- Determination of vertical elevation characteristics and horizontal transfer of radionuclides with burning fuels, fraction composition and disparity of particles.
- Radionuclides wind elevation and transfer models verification.
- Assessment of implementation efficiency of means used for fire extinguishing on radiation contaminated territories.
- Characteristics of radionuclides post-fire distribution in the forest cenosis and assessment of radionuclides transfer out of borders of a fire site.
- Working-out recommendations on stabilisation of a fire situation in Chernobyl Exclusion Zone.

#### **5.Choice of a site for the exercise**

Basic criteria for choice of an experimental site:

- Spatial isolation of an experimental site from basic forest land; it will make impossible extension of a prescribed fire.
- Opportunity for laying sufficient number of fire protection lines.
- Measurable radioactive contamination density, presence of  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  transuranic elements in the composition of fall-outs (V. Poyarkov and D. Robeau, L'accident de Tchernobyl, in book: Catastrophes et Accidents

Nucleaires Dans L' ex-Union Sovietique, EDP Sciences, 2001; Proceeding of International Conference "Fifteen Years after the Chernobyl Accident. Lessons Learned", ISBN 966 7600-01-7, Kiev, 2001; Present and future environment impact of the Chernobyl accident, IAEA-IPSN Study, 1AEA-TECDOC-1240, IAEA, Vienna, 2001; Chernobyl web site, [www.tesec-int.org](http://www.tesec-int.org) updating 2005).

- Opportunity of deployment of a monitoring network around the experiment site.
- A convenient transport communication to an experimental site.

By preliminary assessments, the territory located to the West from the city of Pripyat within the Western trace of the accidental release meets such conditions. Detailed choice of a site could be accomplished during a field examination. Second part of the fire-dangerous period should be considered as an optimum period for the experiment accomplishment (end of summer-beginning of autumn).

## **6. Conclusion**

Chernobyl Exclusion zone forest area provides unique opportunity for studying the mechanism of a release and dispersion of toxic materials during a forest fire. This opportunity has to be used by international community for the benefit of protection against forest fire negative consequences.

### **➤ Risk assessment of forest fire smoke, using Cause-Problem-Symptom analysis**

*(M. Statheropoulos, European Center for Forest Fires, I. Dokas, ADVISES RTN, Universität Paderborn Fakultät für Elektrotechnik, Informatik und Mathematik Institut für Informatik, De, and S. Karma, National Technical University of Athens, Gr)*

## **1. Introduction**

Risk assessment is considered important for addressing effective response actions, so as to manage possible environmental, health, social, economic, or other impacts, caused by stressors. The term *stressor* is assigned to any factor that may cause adverse effects to entities, such as humans, plants or animals; it can be chemical, physical, biological or psychological in nature. The *severity level* of the adverse effects, caused by stressors, is related among others to the stressor and entities characteristics, the stressor distribution in the environment, as well as, the

pathways from the source of the stressor to the entities. Thus, in risk assessment process, those parameters must be clarified and defined.

Forest fires are considered a physical stressor. Until now, there have been some works focusing on forest fire risk assessment (e.g. S.F. McCool et al., *Environ. Management*, 37 (2006) 437). More specifically, guidelines have been prepared, including strategies and policies for management and mitigation of possible impacts caused by forest fires, as well as, public advisories against forest fire smoke (WHO/UNEP/WMO, *Health Guidelines for Vegetation Fire Events - Guideline document*, Lima, Peru, 6-9 October 1998, 1999; US EPA, *Wildfire Smoke: A Guide for Public Health Officials*, University of Washington, 2001; USDA, *Gen. Tech. Rep. RMRS-GTR-42*, 2002; NWCG, *Smoke Management Guide for prescribed and Wildland fire*, 2001).

However, an issue that it seems to gain importance the recent years is the risk assessment of forest fire smoke (ffs). In general, large-scale forest fires produce significant quantities of smoke, which can maintain in the atmosphere for many days, affecting not only the areas in the vicinity of the flame-front but also areas in the dispersion path of the smoke plume. It has been reported that exposure to smoke components, such as particles, acrolein, formaldehyde and CO has been associated with lung function decrements of fire-fighters (J.C. Slaughter et al., *J. Occup. Environ. Hygiene*, 1 (2004) 45) and that communities exposed to ffs during the Southeast Asian forest fires of 1997 experienced short-term increases in cardiorespiratory hospitalizations (J.A. Mott et al., *Int. J. Hyg. Environ. Health*, 208 (2005) 75). Moreover, during a forest fire, the visibility is reduced because of the ffs particles. This can cause numerous irregularities in operation of critical infrastructures (e.g. airports, highways, hospitals) or accidents, i.e. the September 1997 plane crash accident in Sumatra that has been attributed to air traffic control problems during the smog episode, where 234 persons were killed (WHO/UNEP/WMO, *Health Guidelines for Vegetation Fire Events - Guideline document*. Lima, Peru, 6-9 October 1998, 1999). Regarding the environmental impacts of ffs, it has been reported that during the smoke haze of 1997 in Indonesia, atmospheric concentrations of particulate matter, SO<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>, as well as, relative humidity were elevated, whereas photosynthetically active radiation and ambient temperature were reduced (S.J. Davies and L. Unam, *Forest Ecol. Manag.* 124 (1999) 137).

According to literature review, it can be said that there is a need for assessing ffs adverse effects under a standard risk assessment framework and that there are still critical issues that need further investigation and research. More specifically,

mixed exposure of fire-fighters to multiple smoke hazardous compounds, especially when the forest flame-front expands and co-burns other fuels, has to be examined. In addition, it can be concluded that there is a lack of comprehensive studies regarding ffs impacts on infrastructures, e.g. hospitals, army-camps, airports. Enhancement of the existing work regarding environmental impacts of ffs is also necessary.

The main goal of this work is to examine how the Cause-Problem-Symptom analysis (source: [http://www.llnl.gov/es\\_and\\_h/hsm/doc\\_4.07/doc4-07.html](http://www.llnl.gov/es_and_h/hsm/doc_4.07/doc4-07.html)) can be a beneficial tool for the analysis phase of the risk assessment procedure. In order to achieve this goal, a specific structure is followed: Firstly, the risk assessment process is described. Then, the goals and the specifications of the analysis phase are displayed. A description of the Cause-Problem-Symptom analysis, along with an indicative example of ffs risk hypotheses-scenario, is following and the Cause-Problem-Symptom analysis evaluation is presented. Finally, a number of suggestions for possible enhancement of the Cause- Problem-Symptom analysis are given in the conclusion section.

## **2.Risk assessment phases**

An example of a standard risk assessment method is that of a four phases procedure (Guidelines for Ecological Risk Assessment (EPA/630/R-95/002F, April 1998), consisting of: 1) Planning, 2) Problem formulation, 3) Analysis and 4) Risk Characterization phases.

The main goal during the *planning phase* is to point out valuable perspectives and also to define the objectives and management goals of the risk assessment. A management goal can be the protection of specific entities from adverse effects of a stressor, e.g. fire-fighters in the case of ffs chemical stressor.

During the *problem formulation phase*, the purpose of the assessment is articulated, the problem is defined and a plan for analyzing and characterizing risk is determined. Initial work in problem formulation includes the integration of available information regarding sources, stressors, effects, as well as, receptors' characteristics. As a result, two products are generated: assessment endpoints and conceptual models. Assessment endpoints are the valued attributes of entities, upon which risk management actions are focused. Regarding the conceptual model, a major component is the development of a set of risk hypotheses. A risk hypothesis is a specific assumption about potential risk of entities, upon which risk management actions are focused and can be based on theoretical or empirical data, mathematical or probability models.



In the *analysis phase*, the main goal is to determine or predict how the entities, which are under study, are responding, or may respond to stressor exposure. This phase includes two principal activities: characterization of exposure and characterization of effects. For the first, examination of the sources of stressors and their distribution in the environment is required. For the second, evidence for causality and analysis effects, by examining stressor – response relationships, are needed. Both activities evaluate available data for scientific credibility and relevance to assessment endpoints, as well as, to the conceptual models.

*Risk characterization* is the final phase, in which the relations between the stressors, effects and the entities under study are clarified. The goal is to reach conclusions regarding the occurrence of exposure and the adversity of existing or anticipated effects.

This work is focused on the analysis phase of ffs risk assessment process, using the Cause-Problem-Symptom analysis method. An indicative example of a risk-scenario referred to a populated area that is affected by ffs plume is presented; it will be used to test whether the respective ffs data can be organized and structured under the Cause-Problem-Symptom framework effectively.

### **3.Specifications of the analysis phase**

During the analysis phase, the following profiles have to be developed:

*A. A summary exposure profile which:*

- Identifies the receptor.
- Describes the intensity, the spatial and temporal extent of co-occurrence or contact.
- Presents the levels of uncertainty on estimated exposure.
- Reaches a conclusion about the possibility of exposure to occur.

*B. A stressor – response profile that define the:*

- Relationship between stressor levels and adverse effects.
- Plausibility that effects may occur or are occurring, as a result of exposure to stressors.
- Links between measurable adverse effects and assessment endpoints.

*Those specifications can be used as criteria to evaluate the Cause-Problem-Symptom analysis as a supporting tool for the analysis phase.*

## 4. Description of the Cause-Problem-Symptom analysis

### 4.1. Terminology

Figure 1 describes the key elements of Cause-Problem-Symptom analysis. As shown, the objectives of the analysis are to improve and control the risk, which in our case is the ffs and manage its adverse effects. In below, the basic terms of the Cause-Problem-Symptom analysis are explained.

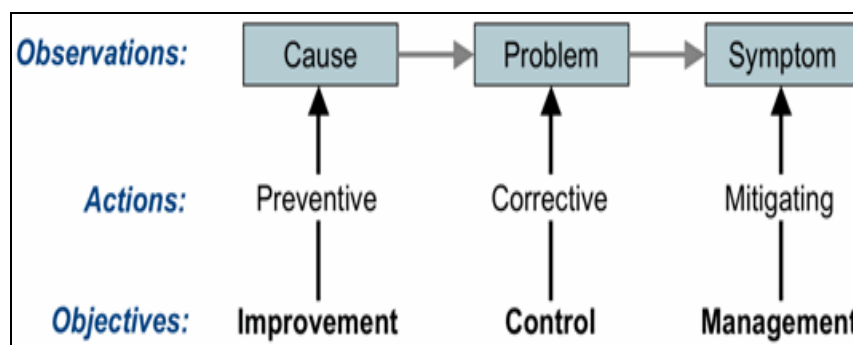


Figure 1: Cause-Problem –Symptom Analysis Elements

(Source: [http://www.llnl.gov/es\\_and\\_h/hsm/doc\\_4.07/doc4-07.html](http://www.llnl.gov/es_and_h/hsm/doc_4.07/doc4-07.html))

#### 4.1.1. Observations

*The analysis begins with the observation of causes, problems and symptoms. Terminology is listed below:*

**Cause:** The events and conditions that contribute to the presence of a problem. Addressing them helps prevent future similar problems.

**Problem:** The specific situation that, if corrected, further symptoms are minimized.

**Symptom:** Undesirable consequences of the problem. Treating them does not eliminate the problem, but may minimize the damage (Environmental Safety and Health Manual, [http://www.llnl.gov/es\\_and\\_h/hsm/doc\\_4.07/doc4-07.html](http://www.llnl.gov/es_and_h/hsm/doc_4.07/doc4-07.html)).

*In the case of Cause-Problem-Symptom analysis application on the ffs risk assessment: 1) the cause is the smoke 2) the problem is that several environmental entities and communities are exposed to ffs and that critical infrastructures are also affected, which leads to 3) a numerous of adverse effects (symptoms).*

#### 4.1.2. Actions

Actions may be of three types: preventive, corrective and mitigating.

**Preventive** actions contribute to reducing the chances that similar problems will occur again. In the case of ffs, there are actions suggested for prevention of ffs episodes.

**Corrective** actions take place for fixing problems directly. In the case of ffs are suggested for controlling the problems that have been observed because of the ffs. Lack or absence of such actions can be possible causes of problems.

**Mitigating** actions take place for countering consequences (symptoms) of problems and in our case are actions to minimize possible symptoms due to ffs.

#### 4.2. Example

An illustrative example of using integrated information regarding ffs and making risk analysis under the Cause-Problem-Symptom framework is that of a big forest fire incident. According to this scenario: 1) a forest fire was burst out under light wind conditions (3-4 m/sec), low relative humidity (RH%<25) and high temperature (>30°C), 2) a smoke convection column was produced, which moved up to a height of 500 m. At this height, the smoke plume was inversed due to moderate wind (6-7 m/sec) and traveled for about 1 hour towards a populated area. As the situation evolved, the wind suddenly turned to strong (10-12 m/sec), which laid down the smoke convection column to the populated area.

The following steps are required for applying the Cause-Problem-Symptom analysis:

- Step 1: Define how the ffs was generated and spread; give characteristics of the stressor.
  
- Step 2: Define the problem caused and give characteristics of the population's exposure.
  
- Step 3: Define the ffs adverse effects on population.
  
- Step 4: Define the preventive actions.
  
- Step 5: Define the control actions.
  
- Step 6: Define the mitigating actions.

Referring to the specific ffs example:

**Step 1:** The source of the stressor (ffs) is the forest fire, which generally can be man-made (anthropogenic) or natural. In the examined case, the forest fire was initiated due to negligence (man-made) and expanded because of the wind (meteorological conditions). The forest was covered with trees and bushes, which characterized by high vegetation density (significant quantity of available forest fuel). No preventive measures have been taken (e.g. application of retardants). FFS stressor is considered a complex mixture of gases liquids and solids; especially when the flame-front expands and co-burns other materials, e.g wastes, ffs becomes even more complex (M. Statheropoulos and S. Karma, FFNet 3 (2005) 6).

**Step 2:** The problem caused by the smoke episode is the exposure of the population to ffs and especially of the sensitive groups, which are considered vulnerable: infants, children, pregnant women, people with cardiorespiratory problems, the elderly. High vegetation density resulted to the generation of significant smoke quantity, which is proportional to the concentration of the pollutants produced (e.g. PM); in such case, the smoke exposure is characterized by high intensity. Dispersion of the smoke plume (ffs distribution), due to the meteorological data, also contributed to the problem caused: the smoke exposure had a significant magnitude (spatial scale). Moreover, the problem is that population and the fire-fighters were exposed simultaneously to multiple hazardous components, as the ffs is considered a complex mixture (mixed exposure).

**Step 3:** Ffs exposure of population might have acute or long-term health effects, such as nose and eye irritation, dizziness, cough and lung function decrease, whereas, long-term effects can be asthma, lung and chest irritation or cancer (US EPA, Wildfire Smoke: A Guide for Public Health Officials, University of Washington, 2000; M. Brauer, Health Guidelines for Vegetation Fire Events-Background Papers, Lima, Peru, 6-9 October 1998, 1999). Generally, in the case of large-scale forest fires, significant quantities of smoke are produced and dispersed to long distances, and hence health effects can be extended from local to regional scale, leading to a significant number of people affected by smoke. For example, during the large-scale forest fires in 1997 in Indonesia, over 12.000.000 of people were affected in Indonesia provinces, plus the population affected by cross border transfer of smoke

(Y. Dawud, Health Guidelines for Vegetation Fire Events-Background Papers, Lima, Peru, 6-9 October 1998,1999).

**Step 4:** The respective preventive actions could be:

- *Early warning of potential fire in high risk days*

Satellite data can be used in order to predict potential fires in high-risk days, by using specific instruments, e.g. the AVHRR instrument of the NOAA (U.S EPA). In addition, fire weather forecasts about fire possibility (WHO/UNEP/WMO, Health Guidelines for Vegetation Fire Events - Guideline document, Lima, Peru, 6-9 October 1998, 1999) can also be used for early warning, by the relevant services.

- *Increase of public awareness*

Civil protection measures and public awareness regarding ffs impacts is a critical factor to achieve prevention of forest fires, especially in the case of anthropogenic forest fires. Smart displays, warning about the potentiality of a forest fire, can be used as a tool for civilians' preparedness in high-risk days.

- *Retardants' use*

In order to prevent forest fires expansion, chemicals can be used, called long-term forest fire retardants (Extended Retardants Application Systems (ERAS) project, EVG1-2001-00019). These chemicals are applied on forests before the high risk summer period and they act as reducers of the evolution temperature of volatiles, produced from the pyrolysis of wood, in order to prevent auto-ignition of those volatiles.

- *Classification of ffs components*

Information about the possible chemical composition of ffs, taking into consideration the flame-front expansion e.g. to rural fields, could be a beneficial tool for indications of possible pollutant types that are expected to be found in the smoke. Possible scenarios of forest flame-front expansion and classification of ffs components are presented in the format of a road-map for preliminary air-quality assessment in a forest fire elsewhere (M. Statheropoulos and S.Karma, FFNet, 3 (2005) 6).

**Step 5:** The corrective-control actions that can be used are:

- *Suppression of forest fire*

To control ffs episode, direct suppression of forest fire is required, by using ground, aerial or other means (short-term retardants use). The cost of such

investment on means and methods is correlated to the characteristics of receptor's exposure to ffs, such as frequency and periodicity of forest fires.

- *On-line monitoring of air-quality in the affected areas during the smoke episode*

Air-quality monitoring in a forest fire is critical in order to determine concentrations of the smoke pollutants. Analytical instruments have been used for monitoring smoke and aerosols, generated by forest fires (W.B. Grant, Health Guidelines for Vegetation Fire Events - Guideline document Lima, Peru, 6-9 October 1998, 1999). However, the main limitation of such instruments was that the analysis of samples could not be done on-line in the field, but had to take place in the laboratory. Field sampling in a forest fire incident needs fast moving, high-speed separation of the ffs complex mixture and quick estimation of real-time data, in order to address effective emergency response plans and protective measures for the operational people and the exposed population. Hyphenated instruments e.g. GC-MS, GC-IMS, GC-GC, for monitoring volatiles and gases, as well as, ATOFMS for the on-line chemical analysis of particles, offer such benefits. Specifications of portable units and devices for monitoring air-quality in a hostile and heavy environment, such as the one in a forest fire, are presented elsewhere (A. Agapiou, FFNet, 3 (2005) 26). Simple sensors (e.g. CO<sub>2</sub>, CO, NH<sub>3</sub>) can also be used, but cross sensitivities should be taken into consideration. Existing air pollution monitoring stations could be equipped with the proper instruments, in order to provide operational centers with air-quality reports in a forest fire incident e.g. PM levels reports.

- *Early detection of ffs*

Early detection of ffs is critical in order to suppress forest fire on-time and cope with the smoke expansion. This can be achieved by using satellite data (GIS) and LIDAR (Light Detection and Ranging) techniques. LIDAR has been recently used in the 2002 Canadian Forest Fires, in order to determine the existence of the smoke plume above Baltimore (A. Sapkota et al., Environ. Sci. Techn., 39 (2005) 24).

- *Prediction of the smoke plume path*

Another corrective action is the use of models of ffs dispersion, in order to estimate smoke plume path and decide on the areas that will be affected, before the smoke plume approach. Such Information is essential in order to take on time the proper measures (e.g. close part of a highway). Evaluation of smoke dispersion from forest fire plumes, using LIDAR experiments and modeling, has been reported (A. Lavrov, International Journal of Thermal Sciences, In press). An integrated numerical

system to estimate air-quality effects of forest fires has also been tested (A.I. Miranda, Inter. Journal of Wildland Fire, 13 (2004) 217). Satellite data can also be used for identify dispersion of smoke plume.

- *Estimation of mixed exposure*

In order to estimate mixed exposure, due to the complexity of ffs, empirical models can be used, such as the Em assessment criterion. According to this approach, values of Em more that 1 are considered critical (I. Morioka et al., Arch. Environ. Health, 54 (1999) 341).

- *Emergency doctors, especially for high risk population*

A number of medical doctors can be attributed especially to the sensitive groups (high risk population), in emergency situations.

**Step 6:** Mitigating actions can be the:

- *Use of personal protective equipment (PPE)*

Personal protective equipment, such as simple half-face masks, can be distributed to the exposed population. It should be noted that such masks, do not offer complete protection from the smoke components, but only a partial protection from coarse particles inhalation.

- *Evacuation of the area*

In very smoky conditions, half-face masks might not be effective, especially for the sensitive groups. For that reason, early evacuation of place, before the smoke plume's approach, might be needed. It should be noted that exposure limits for population and sensitive groups, as well as, evacuation criteria are need to be considered (FFNet, 3 (2005) 36).

- *Stay indoors*

Stay indoors and use air-cleaners are some of the suggested measures for the population, in order to mitigate symptoms of smoke (U.S EPA, Wildfire Smoke: A Guide for Public Health Officials, 2001).

- *Admission to hospitals*

Early admission to hospitals of the patients is critical in order to avoid worsening of the symptoms or even death, especially of the sensitive groups (e.g. the elderly).

The application of Cause-Problem-Symptom analysis presented above is resumed in Table 1.

Table 1. Cause-Problem-Symptom analysis applied on ffs, for a population affected by the smoke plume.

<b>Cause</b> (How the ffs was generated? What are the characteristics of the stressor?)		<b>Problem</b> (Characteristics of population's exposure to ffs)		<b>Symptoms</b> (Possible adverse effects of ffs )	
<b>Observations</b>	<b>Preventive Actions</b>	<b>Observations</b>	<b>Corrective Actions</b>	<b>Observations</b>	<b>Mitigative Actions</b>
Source of ffs: a man-made caused forest fire	-Early warning of potential fire in high risk days -Increase of public awareness	Exposure of sensitive groups (e.g. children, the elderly) to ffs	Emergency doctors, especially for high risk population	-Acute effects e.g. breathing problems, suffocation -Long term effects e.g. asthma, cardiopulmonary disorders, death	-Early admission to hospitals if needed  -Early evacuation to safe place  -Distribution of masks
Forest with high vegetation density	Use of long-term retardants or other measures to prevent expansion	-Significant quantities of smoke-High concentration of pollutants e.g. PM (intensity)	-Suppression of fire by ground and aerial means  -On-line monitoring of PM concentration	Significant number of population affected (regional scale of health effects)	-Stay indoors  -Early evacuation of village
Meteorological conditions: strong wind, low RH%, High T°, sun radiation	Weather Forecast	Dispersion of smoke plume - significant magnitude of exposure (spatial scale)	-Early detection of ffs  -Prediction of the smoke plume path		-Distribution of masks
FFS: a complex mixture of pollutants	Classification of smoke components (road-map)	Exposure of population and the fire-fighters to multiple pollutants	-Tools for risk estimation of mixed exposure (e.g. empirical models)	-Acute effects e.g. cough, eye & nose irritation  -Long term effects e.g. asthma, pulmonary diseases	-Use of masks  -Stay indoors  -Evacuation of place



## **5.Evaluation of the Cause-Problem-Symptom analysis**

Specifications of the analysis phase, presented in section 3, will be used as criteria to evaluate the Cause-Problem-Symptom analysis.

Regarding the development of exposure profile, identification of possible receptors is feasible, by using one (e.g. Table 1), or multiple Cause-Problem-Symptom analysis tables. More specifically, the stressor's pathway to each receptor, as well as, the intensity, spatial and temporal extent of co-occurrence or contact can be assumed in the "Cause" and "Problem" columns, respectively (see Table 1). However, if there is a need for a more detailed description of the above parameters, the use of another method is probably recommended. Description of the levels of uncertainty on estimated exposure can be made only linguistically. Cause-Problem-Symptom analysis can help risk assessors to reach a conclusion about the possibility of exposure to occur in a qualitative way.

Regarding the development of stressor – response profile, the relationship between stressor levels and adverse effects, as well as, the plausibility that effects may occur or are occurring as a result of exposure to stressors, can be described in the "Symptom" column of the Cause-Problem-Symptom analysis table. Links between measurable adverse effects and assessment endpoints are feasible by using this method; future work can be the addressing of ffs assessment endpoints and definition of their relation to the adverse effects.

Cause-Problem-Symptom analysis is easy to comprehend; the gathered data can be easily classified at the three main columns of the analysis table (Cause-Problem-Symptom). Using the appropriate software (e.g. spreadsheets), the maintenance and updating processes can be accomplished. While performing the analysis, the addressing of preventive, corrective and mitigating actions to the respective cause, problem and symptoms, is required. This is quite important, as long as it helps risk assessors to organize better the available information and propose actions for coping with the stressor's effects.

## **6.Conclusions**

The scope of a risk assessment is to help decision makers to define control and mitigating actions against the anticipated adverse impacts of stressors. Risk assessment of ffs is considered critical the recent years. This work is focused on the analysis phase of ffs risk assessment process, by using the Cause-Problem-Symptom analysis. After evaluating the analysis, it seems that:

- Cause-Problem-Symptom analysis can be considered easy to use and comprehend.

- The relation between the stressor's pathways to receptors and the adverse effects can be defined in a satisfactory level.
- It can be used to increase the productivity of the risk assessors.
- The Cause-Problem-Symptom analysis tables have been modified to integrate all the required information for the development of the exposure and stressor – response profiles.

According to the above, Cause-Problem-Symptom analysis in general, can significantly facilitate risk assessors during the risk analysis phase. In the case of the analysis application on ffs, the respective tables can be developed if it will be applied on a number of possible ffs risk hypotheses-scenarios. This elaborated version can be a useful operational tool for the relevant services (e.g. fire-brigades).

## **7.Acknowledgements**

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## ***Session 4: Summary of the discussion and comments of the participants***

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In this workshop, critical issues regarding ffs were extensively discussed, as well as, expertise and know-how were exchanged among the participants. The following comments are the summary of those made during the extended discussions that took place at the end of the sessions.

Firemen should be aware of the heavy environment of the front-line during a forest fire. Field portable instruments can provide with critical information regarding air-quality in the forest flame-front, so as to prevent exposure of fire-fighters to high concentrations of hazardous and toxic smoke components. During a forest fire, dynamic phenomena take place and very rapid changes of concentration profiles in space and time usually occur. The environment is characterized as “heavy and hostile” for the exposed people (fire-fighters), due to the high temperatures and also to the soot and tars produced (*M. Statheropoulos*).

Fast response detectors can be integral part of a uniform (miniaturized instruments) or can be carried by the firemen for their own safety (*W. Vautz*).

The chemical detectors are mainly used for monitoring vapors. It is also very important to monitor possible radiation. Burning of forests with high concentration of radionuclides, such as in Chernobyl Exclusion Zone, is considered to contribute with significant emission of radiation. The particulate matter produced in such case can absorb radiation and be transferred to very long distances (*V. Poyarkov*).

There are instruments that can determine in real-time the size and chemical composition of particles. Among them are the Aerosol Time-of-Flight Mass Spectrometers (ATOFMS) (*E. Filimundi*).

On-line monitoring in the field, by using state of the art technologies, is a critical issue. However the number of persons and specialization needed to operate field instruments has to be taken into consideration (*F. Pla*).

A remote station can be used as command center, where the data processing would take place and then the results would be diffused as a signal alert to the firemen, through a network. In that way, the number of operators with expertise needed is minimized. As long as humans cannot be exposed to temperatures higher than 60-70°C, portable field detectors carried by the fire-fighters near the flame-front will be exposed to those temperatures. Moreover, in order to protect detectors from total suspended particles, an impactor or filter can be used in front of them (*N. Arnold*).

Clinical toxicology is needed in order to assess fire-fighter's symptoms after exposure to forest fire smoke (ffs). The fact that ffs is a complex mixture makes the ffs exposure assessment more difficult and for that reason specialized doctors are needed (*G. Seynaeve*).

Risk assessment of ffs is essential in order to define possible adverse effects on receptors, such as communities, infrastructures and the environment and to address the respective preventive, corrective and mitigating actions. Further research is needed towards this direction in order to develop a useful operational tool for the fire-fighters (*S. Karma*).

## **Session 5: Table-top exercise scenarios**

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### ➤ **KAPNOS fire-scenarios**

***(P. Theodorou, General Secretary of Civil Protection, Ministry of Interior, Gr, M. Statheropoulos, European Center for Forest Fires and S. Karma, National Technical University of Athens, Gr)***

In this session, KAPNOS fire-scenarios are presented. These are simplified working scenarios referred to a forest fire smoke incident, which can facilitate the discussion session.

### **1. Introduction**

The scenarios prepared with the following objectives:

- Discuss procedures for field measurements.
- Present advantages and limitations of different field chemical analysis methods.
- Propose field instrument specifications.
- Reflecting on all issues of crisis management (personnel and population protection, critical infrastructure operation, communication, responsible and reliable monitoring).

### **2. Description of the scenarios**

The scenarios take place in the X region of X-land. Demographic data and a map of the region are given. The forest fire smoke incident starts at the Peak Mountain during the afternoon and lasts for two days.

More specifically:

#### **Demographic data:**

**Country:** X-land, 15.000.000 population.

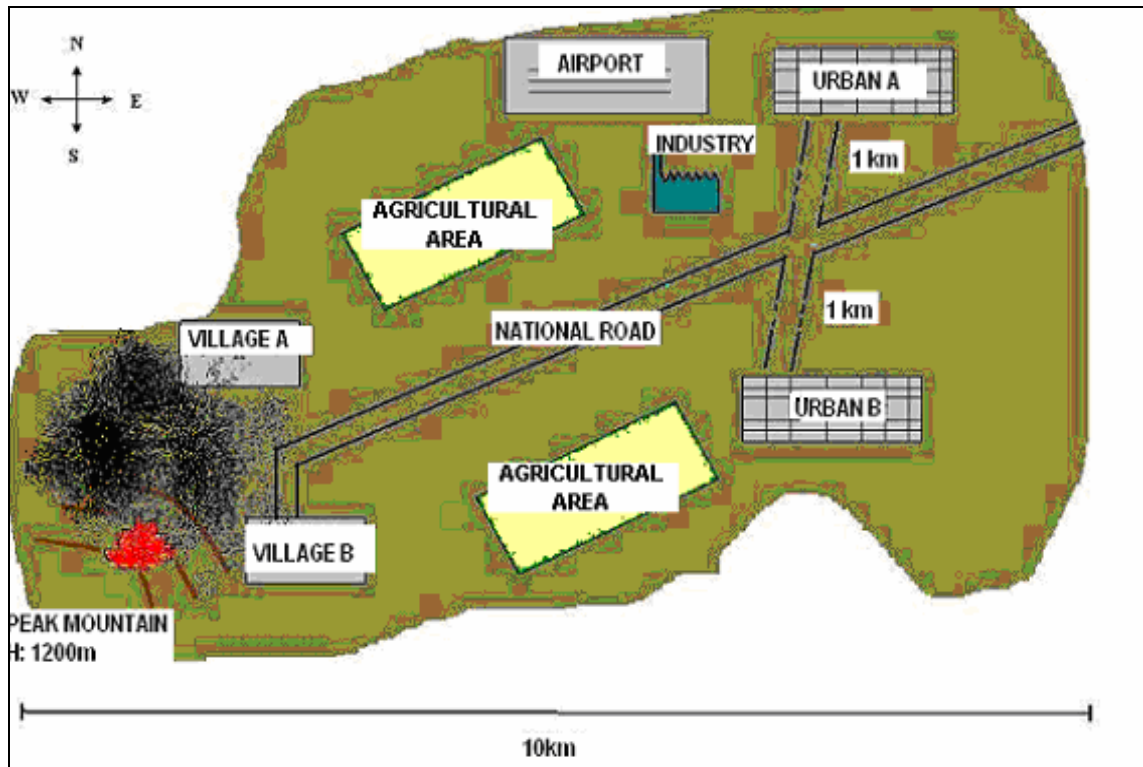
**Forest fire affected area:** A region of approximately 600.000 population, with limited industrial/ commercial activities and mostly agricultural. Recreational facilities near the Peak Mountain exist.

**Cities:** Urban A, 500.000 population.

Urban B, 100.000 population.

**Villages :** Village A, 5.000 population.

Village B, 2.000 population.



*Map of the Region*

**Forest fire characteristics:**

**Peak Mountain:** 1.200 m height, slopes mostly >30%.

**Total forest area:** 5.000 hectares.

**Cause of fire:** Negligence.

**Area burned:** 1.000-1.500 hectares.

**Ignition point:** at 150-200m height of the Peak Mountain forest.

**Time:** 3:00 p.m.

**Meteorological Data:** 32 °C, RH%<25.

**Fire front spread:** 5 km/h.

### **Forest fire smoke scenarios:**

- **KAPNOS 1**

**Initial wind:** W, 3-4 m/sec (light wind).

**Description of the incident:**

A convection column of smoke is produced, moving up to a height of 500 m. At this height, the smoke plume is inversed by a moderate wind of 6-7 m/sec and is travelling to the East. In about 1 h, it reaches the Urban area A. The wind turns suddenly from moderate to strong (12 m/sec) and this causes a lay down of the smoke to the urban area.

The areas mainly affected are the Urban A, the Industrial region and the National Road.

**Topics to discuss:** Urban population exposure to smoke plume; reduced visibility; possibility of photochemical reactions; how to do monitoring of air-quality in these areas; crisis management issues.

- **KAPNOS 2**

**Initial wind:** W, 3-4 m/sec (light wind).

**Description of the incident:**

A convection column of smoke is growing up, following the terrain of the Peak Mountain, reaching a height of 2 km. At this height, suddenly the wind change to moderate-strong (8-9m/s), so that down-slope wind lays down the smoke convection column to the downwind site of the mountain, where the Village B is situated.

The areas affected are Village B (mainly), Village A and a part of the National road.

**Topics to discuss:** Air-quality monitoring; crisis management; village population and ground fire-fighting forces exposure to smoke plume; reduced visibility; how to do monitoring of air-quality near the fire front; possible evacuation of village B (if yes, all the population or specific groups?); necessary PPE for fire-fighters and population.

- **KAPNOS 3**

**Initial wind:** S, 4-5 m/s (moderate).

**Description of the incident:**

A convection column of smoke is moving up at a height of 300 m and is travelling to North for about 45 min, with moderate wind. At this time wind changes to SW, so that the plume is transferred to the airport, in a total time of about 1,5 h from the beginning of the fire. The wind turns suddenly from moderate to strong (12 m/sec), causing a lay down of the smoke convection column to the airport.

The areas affected are the airport, as well as, Villages A, B and the National road.

**Topics to discuss:** Air-quality monitoring; reduced visibility; crisis management.



## **Appendix**

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### ➤ **Glossary**

#### **Additivity<sup>1</sup>**

When the effect of the mixed exposure is equal to the sum of the effects of the individual components. Effect may be referred to the measured response or the incidence of adversely affected species.

#### **Biomarkers<sup>1</sup>**

Indicators of exposure, measured in biological samples or systems. Biomarker measurements have a high potential value because they are made with human samples, e.g. ETS (Environmental Tobacco Smoke) biomarkers.

#### **Complex mixture<sup>1</sup>**

A mixture containing so many components that any estimation of its toxicity, based on its components' toxicities contains too much uncertainty.

#### **Exposure Limits by various Health Organizations**

- TLV-ACGIH (TWA, 8 h/d)(*Threshold Limit Value - American Conference of Governmental Industrial Hygienists, Time-Weighted Average*)
- PEL – OSHA (TWA, 8 h/d)(*Permissible Exposure Limit - Occupational Safety and Health Administration, Time-Weighted Average*)
- REL- NIOSH (TWA, 10 h/d)(*Recommended Exposure Limit - National Institute for Occupational Safety and Health-Time Weighted Average*)

#### **LD50<sup>1</sup>**

Lethal Dose of a compound for 50% of the animals exposed.

#### **Mixed exposure<sup>1</sup>**

It is exposure to either chemical mixtures, different substances at different times, simultaneous exposure to multiple substances, or simultaneous exposure to a chemical substance and another stressor.

## **Synergism<sup>1</sup>**

When the toxic effect of the mixed exposure is greater than that suggested by the component toxic effects.

<sup>1</sup> NIOSH publication No. 2005-106, *Mixed exposures Research Agenda - A report by the NORA Mixed Exposures Team*.



