Doctoral School in Environmental Engineering – 28th Cycle

Development of criteria for the minimization of the impacts of underestimated pathways of human exposure to atmospheric pollutants

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ΔP: Pressure drop [mmH_2O].

ΔPOP_{air}: Ratio between the POP concentration in air after and before the exposure increase [-].

ΔPOP_{faeces}: Ratio between the POP concentration in the faeces after and before the exposure increase [-].

$\Delta POP_{food,loc}$: Ratio between the POP concentration in the locally produced food after and before the exposure increase [-].

$\Delta POP_{food,nloc}$: Ratio between the POP concentration in the non-locally produced food after and before the exposure increase [-].

ΔPOP_{in}: Ratio between the intakes by the human body after and before the exposure increase [-].

ΔPOP_{other}: Ratio between the POP concentration in the sludge from the unexposed population whose wastewater is collected at plant A after and before the increase in the exposure of the target population [-].

ΔPOP_{sludge}: Ratio between the POP concentration in the sewage sludge after and before the exposure increase [-].

Φ: Ratio between the air concentration of contaminant bound to particles and the total air concentration [-].

ρ_a: Air density [kg m^{-3}].

A: Area of the transversal section [m^2].

A_g: Average area daily grazed by one cow [m^2].

$ADAF$: Age-dependent adjustment factor [-].

AT: Averaging time [y].

BW: Body weight [kg].

b_{bf}: Pollutant bioavailability in beef fat [-].

b_{mf}: Pollutant bioavailability in milk fat [-].

B_{vpa}: Air-to-leaves transfer factor [-].

BCF_e: Concentration factor of the egg yolk [-].

BCF_p: Soil-to-plant concentration factor [-].

c: Junge's constant [atm cm].

C: Concentration [mg m^{-3}, multiples or submultiples].

C_a: Ambient air concentration [mg m^{-3}, multiples or submultiples].

$C_{a,g}$: Ambient air concentration of the gas-phase pollutant [mg m^{-3}, multiples or submultiples].

$C_{a,p}$: Ambient air concentration of the particle-phase pollutant [mg m^{-3}, multiples or submultiples].

C_{bf}: Total concentration of pollutant in beef fat [pg (TEQ) kg^{-1}].

C_e: Total concentration of pollutant in eggs [pg (TEQ) kg^{-1}].

C_{fg}: Total concentration of pollutant in fodder or grain [pg (TEQ) kg^{-1}].

$C_{food,loc}$: Percentage of the consumption of locally produced food [%].

$C_{food,nloc}$: Percentage of the consumption of non-locally produced food [%].

c_g: Fraction of A_g covered with grass [-].

C_g: Total concentration of pollutant in grass [pg (TEQ) kg^{-1}].

C_{in}: Inlet concentration of pollutant [mg m^{-3} or ppm].

C_{mf}: Total concentration of pollutant in milk fat [pg (TEQ) kg^{-1}].

C_{out}: Outlet concentration of pollutant [mg m^{-3} or ppm].

$C_{p,as,f}$: Total concentration of pollutant in fruit through uptake from air and stem [pg (TEQ) kg^{-1}].

$C_{p,dg}$: Total concentration of pollutant in plant by dry gaseous deposition [pg (TEQ) kg^{-1}].

$C_{p,p}$: Total concentration of pollutant in plant by particle deposition [pg (TEQ) kg^{-1}].

$C_{p,r}$: Total concentration of pollutant in plant by root uptake [pg (TEQ) kg^{-1}].

$C_{p,r,f}$: Total concentration of pollutant in fruit through root uptake [pg (TEQ) kg^{-1}].

$C_{r,g}$: Gaseous-phase concentration of pollutant in the raindrop [pg m^{-3}].

$C_{r,p}$: Particle-phase concentration of pollutant in the raindrop [pg m^{-3}].

C_s: Total soil concentration of pollutant [pg (TEQ) kg^{-1}].

D: Total daily atmospheric deposition [pg (TEQ) m^{-2} d^{-1}].

D_d: Dry deposition [g m^{-2} d^{-1}, multiples or submultiples].

D_{LT}: Long-term total atmospheric deposition [pg (TEQ) m^{-2} y^{-1}].

D_w: Wet deposition[g m^{-2} d^{-1}, multiples or submultiples].

E: Exposure [mg kg^{-1} y^{-1}, L kg^{-1} y^{-1} or m^3 kg^{-1} y^{-1}].

$EBRT$: Empty bed residence time [s]

EC: Elimination capacity [g m^{-3} h^{-1}].

EC_{max}: Maximal elimination capacity [g m^{-3} h^{-1}].

ED: Exposure duration [y].

EF: Exposure frequency [d y^{-1}].

Ey: Energy yield [g kW^{-1} h^{-1}].

Ey_{max}: Maximal energy yield [g kW^{-1} h^{-1}].

$f_{f,b}$: Fraction of fat in beef [-].

$f_{f,d}$: Fraction of fat in dairy products [-].

$f_{f,m}$: Fraction of fat in cow's milk [-].

F_{fg}: Fraction of the chicken's diet that is fodder or grain [-].

F_g: Fraction of the chicken's diet that is grass [-].

f_p: Fraction of total air concentration sorbed to particulates at 293 K [-].

F_s: Fraction of the chicken's diet that is soil ingestion [-].

f_v: Fraction of total air concentration in vapour phase at 293 K [-].

$f_{y,e}$: Average mass fraction of yolk in the egg [-].

h_p: Precipitation rate [mm d^{-1}, multiples or submultiples].

$I_{c,s}$: Average daily soil ingestion by cows [kg d^{-1}].

$I_{h,b}$: Average daily consumption of beef by humans [kg d^{-1}].

$I_{h,d}$: Average daily consumption of dairy products by humans [kg d^{-1}].

$I_{h,e}$: Average daily consumption of eggs by humans [kg d^{-1}].

$I_{h,f}$: Average daily fruit consumption by humans [kg d^{-1}].

$I_{h,s}$: Average daily soil ingestion by humans [kg d^{-1}].

$I_{POP,food}$: Percentage of POPs taken in by food consumption [%].

$I_{POP,inhal}$: Percentage of POPs taken in by inhalation [%].

IR: Intake rate [mg d^{-1}, L d^{-1} or m^3 d^{-1}].

IR_c: Intake rate of a pollutant by cows [pg (TEQ) d^{-1}].

$IR_{c,g}$: Intake rate of a pollutant by cows through consumption of grass [pg (TEQ) d^{-1}].

$IR_{c,s}$: Intake rate of a pollutant by cows through accidental soil ingestion [pg (TEQ) d^{-1}].

$IR_{h,b}$: Intake rate of a pollutant by humans through consumption of beef [pg (TEQ) d^{-1}].

$IR_{h,e}$: Intake rate of a pollutant by humans through consumption of eggs [pg (TEQ) d^{-1}].

$IR_{h,f}$: Intake rate of a pollutant by humans through consumption of fruit [pg (TEQ) d^{-1}].

$IR_{h,md}$: Intake rate of a pollutant by humans through consumption of milk and dairy products [pg (TEQ) d^{-1}].

$IR_{h,s}$: Intake rate of a pollutant by humans through accidental soil ingestion [pg (TEQ) d^{-1}].

$IR_{h,v}$: Intake rate of a pollutant by humans through consumption of vegetables and cereals [pg (TEQ) d^{-1}].

k: Mean annual soil dissipation rate [y^{-1}].

k_p: Loss rate for the plant surface particles [y^{-1}].

$L_{h,b}$: Ratio of beef coming from the contaminated area to the total beef consumed by humans [-].

$L_{h,e}$: Ratio of eggs coming from the contaminated area to the total eggs consumed by humans [-].

$L_{h,d,l}$: Ratio of dairy products coming from the contaminated area to the total dairy produced consumed by humans [-].

$L_{h,f}$: Ratio of fruit coming from the contaminated area to the total fruit consumed by humans [-].

$L_{h,m}$: Ratio of milk produced from the contaminated area to the total milk consumed by humans [-].

$L_{h,v}$: Ratio of vegetables coming from the contaminated area to the total vegetables consumed by humans [-].

M: Soil mixing mass [kg m^{-2}].

ML: Mass loading rate [g m^{-3} h^{-1}].

P: Discharge power [W].

P_m: Average daily milk production [kg d^{-1}].

P_{mf}: Average daily production of milk fat [g d^{-1}].

$P_{s,j}$: Saturation vapour pressure of sub-cooled liquid [atm].

Q_g: Gas flow rate [m^3 h^{-1}, multiples or submultiples].

Q_l: Liquid flow rate [L h^{-1}, multiples or submultiples].

R: Risk [-].

R_p: Interception rate of particles by the vegetation [-].

RE: Removal efficiency [%].

RE_{max}: Maximal removal efficiency [%].

RE_{NTP}: Removal efficiency of the non-thermal plasma treatment [%].

$RE_{NTP,max}$: Maximal removal efficiency of the non-thermal plasma treatment [%].

RfC: Reference concentration [mg m^{-3}].

RfD: Reference dose [mg kg^{-1} d^{-1}].

RH: Relative humidity [%].

S_g: Scavenging ratio related to the contaminant in the dissolved phase in the raindrop [-].

S_p: Scavenging ratio related to the particle-bound contaminant in the raindrop [-].

S_t: Surface area of the particle [cm^2 cm^{-3}].

S_{tot}: Total scavenging ratio [-].

SCO_2: Selectivity to CO_2 [%].

SED: Specific energy density [J L^{-1}].

SF_{inhal}: Inhalation slope factor [(mg kg^{-1} $d^{-1})^{-1}$].

SF_{oral}: Oral slope factor [(mg kg^{-1} $d^{-1})^{-1}$].

SL: Surface loading rate [m^3 m^{-2} h^{-1}].

t: Time [y].

T: Animal lifetime [y].

t_d: Time since D_{LT} has been achieved [y].

t_m: Number of milk producing days per year [d y^{-1}].

t_p: Exposure time of the vegetation to deposition per single harvest [y].

UR_{inhal}: Inhalation unit risk [(µg $m^{-3})^{-1}$].

UR_{oral}: Ingestion unit risk [(µg $L^{-1})^{-1}$].

V: Volume [m^3, multiples or submultiples

V_d: Total dry deposition velocity [cm s^{-1}].

V_{dg}: Dry gaseous deposition velocity [cm s^{-1}].

V_p: Dry particle deposition velocity [cm s^{-1}].

Y_p: Aerial biomass of grass [kg m^{-2}].

Abstract

Air pollution is still the cause of several diseases, among which cancer is often associated to excessive or anomalous exposure to air pollutants. In addition to well-known sources of emission of air pollutants, several activities are still unregulated or not adequately controlled by conventional removal technologies; furthermore, the presence of local criticalities may elude the conventional monitoring approach. This thesis aims at providing new options to detect anomalous situations of exposure and to minimize the impacts of air pollutants by acting on two different levels: the prevention of excessive intakes and the prevention of emissions into the atmosphere. Carcinogenic organic air pollutants will receive special attention in this thesis.

After a short introduction to the topic, in the second chapter of this thesis, potential critical situations of exposure are presented, with a special focus on two of the most potent carcinogenic air pollutants: dioxin and benzene. Open issues regarding both the lack of regulations for some activities and the inadequacy of some conventional monitoring approaches are described. Proposals for integrative monitoring techniques and methodologies for exposure assessment are then briefly presented. Four of them were developed during this doctoral research and are described in more details in the third chapter of this thesis; the purpose of these methodologies is to offer additional tools to detect anomalous situations of exposure to air pollutants, in both rural and urban contexts, and to estimate the dominant source of exposure to specific compounds in an area. The fourth chapter is dedicated to presenting a proposal for a limit value of dioxin deposition to soil. Dioxin are able to accumulate in the food chain; therefore, this chapter presents the development of a reverse food-chain model, starting from the Tolerable Daily Intake proposed by the World Health Organization, running through the food chain backwards on the basis of the diet of a population and determining a safe value to preserve fields and pastures. Such method represents an attempt to overcome the current absence of a regulatory limit value for atmospheric deposition of dioxin to soil. This approach aims at reducing the potential exposure to dioxin by preventing excessive intake. In the fifth chapter, a critical analysis on biofilters is carried out. Biofilters are a specific kind of air pollution control technology, widely used to treat air streams with low concentrations of volatile organic compounds (VOCs). Biofilters may be inefficient under unsteady conditions of inlet loading rate; in addition, when treating high flow rates, biofilters cannot guarantee a proper dilution of the plume in the atmosphere, due to intrinsic design reasons. Biotrickling filters (BTFs) are here presented in a review as a more efficient alternative; the improvements in air quality obtained when replacing a biofilter with BTFs are also highlighted through dispersion simulations. This chapter aims at proposing an alternative to reduce exposure directly at the emission level, rather than at the receptor level. The same aim is pursued in the final part of this thesis, in which an innovative VOC removal technology is studied: non-thermal plasma (NTP). Two laboratory activities are presented: initially, NTP is applied to treat two mixtures of air and VOCs, chosen to represent typical emissions from real industrial activities; the positive results in terms of VOC removal and the partial formation of more soluble byproducts led to a second experimental activity in which NTP was applied as a pre-treatment to a biofilter. NTP revealed to be a promising option to manage peaks of inlet loading rate, which biofilters are often subject to in real cases.

1 Introduction

One of the most simple and, meanwhile, comprehensive definition of human exposure was formulated by the U.S. National Academy of Sciences (NAS), according to which human exposure is defined as *"an event that occurs when there is contact at a boundary between a human and the environment with a contaminant of a specific concentration for an interval of time"* (NAS, 1991). The effects of exposure depend on three combined factors: the type of pollutant, the duration of exposure and the concentrations the single individual is exposed to. Human beings can be exposed to both carcinogenic and non-carcinogenic compounds in many circumstances. Short-term exposure to high concentrations of a pollutant can induce acute effects, causing illness, worsening of previously arisen pathologies and, eventually, death, depending on the pollutant itself and on the peak concentrations. Contrarily to these exceptional episodes of exposure, long-term exposure to lower concentrations can pose a hidden threat to human health, since the symptoms may arise after years or decades. Long-term exposure is particularly risky when the individual is exposed to carcinogenic contaminants. With regards to air contaminants, there is a variety of unregulated emission sources and underrated situations of exposure to atmospheric pollutants that may represent a hidden hazard for humans.

1.1 Priority pollutants

Identifying the priorities of intervention is particularly useful to decision-makers to understand what solutions (technical or political) should be adopted and to estimate the related costs. Due to the socio-economic and health impact of chronic diseases, special attention should be given to mitigating the role of underestimated exposure pathways that imply long-term exposure to air pollutants.

Cancer is one of the types of chronic diseases induced by air pollution. 14.1 million new cases and 8.2 million deaths from cancer were estimated to occur worldwide in 2012 (Ferlay et al., 2015). In addition to the social costs related to cancer, huge monetary costs are involved for medical assistance of patients. As an example, in the United States, the medical expenses to treat cancer in 2011 accounted for $ 88.7 billion (American Cancer Society, 2015). Incidence and mortality of the majority of cancer types are increasing in several developing countries (Jernal et al., 2010), due to different possible reasons: unhealthy lifestyles, smoking and uncontrolled industrial and economic development, with increasing number of sources of environmental pollution in the industrial, energy and transportation sectors.

In determining target pollutants to focus on, priority should be given to carcinogenic compounds, since death is still a frequent consequence of cancer. By reducing the impact of long-term exposure and monitoring the proper operation of the adopted mitigation strategies, the occurrence of acute exposure episodes would be consequently limited.

Table 1.1 reports the most common air pollutants classified by the International Agency for the Research on Cancer (IARC) as demonstrated carcinogens for humans, belonging to Group 1 (IARC, 2015a). Heavy metals, like chromium VI (Cr VI), cadmium (Cd), arsenic (As), nickel (Ni), are emitted by a smaller number of sectors, mostly by point sources belonging to the metallurgical industry, the combustion of fossil fuels and the incineration of waste (Wu et al., 1999). Organic compounds, like polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), benzene, benzo[*a*]pyrene, formaldehyde, 1,3-butadiene and trichloroethylene, are emitted by a larger variety of sectors and mainly by area sources (Wu et al., 1999). Recent studies highlighted that the incidence of organic carcinogens in the total cancer risk that can be induced in a target population is greater than the incidence of carcinogenic metals (Logue et al., 2011; Wu et al., 2011). This is particularly evident in the urban environment, although the dominance of organic carcinogens, even at regional scale, is also documented (Kadlec, 2008).

1.2 Aims of this research

The focus on underestimated emission sources and mechanisms of exposure has the purpose of stressing the need for a routine monitoring of such situations, highlighting incongruities between some limit values set by the legislation and the corresponding cancer risk deriving from exposure. The proposals for new methods for exposure assessment and for new or updated limit values would limit the exposure and, thus, would act on the side of prevention at the receptor level. In addition, new design criteria for specific plants responsible for emissions and improved air treatment systems would act directly on the side of prevention at the emission level.

Table 1.1: Most common air pollutants classified in Group 1 by the IARC (IARC, 2015a, 2016).

Substance	Organic/Inorganic	Carcinogenic effects
Formaldehyde	Organic	Leukaemia and cancers of nasal sinuses and nasopharynx
Benzo[*a*]pyrene	Organic	Recently updated to Group 1 based on mechanistic and other relevant data; epidemiological data on humans are still lacking
Benzene	Organic	Leukaemia, non-Hodgkin lymphoma, kidney and lung cancers
Vinyl chloride	Organic	Angiosarcoma of the liver, hepatocellular carcinoma, lung cancer and malignant neoplasms of connective and soft tissues
Trichloroethylene	Organic	Non-Hodgkin lymphoma, liver and kidney cancers
1,3-Butadiene	Organic	Leukaemia and malignant lymphoma
Polychlorinated biphenyls	Organic	Recently updated to Group 1; report in preparation
Polychlinated dibenzo-*p*-dioxin	Organic	Lung cancer, soft-tissue sarcoma, non-Hodgkin lymphoma, digestive system cancer, multiple myeloma
Arsenic	Inorganic	Cancers of lung, urinary bladder and the kidney, skin, liver and prostate
Beryllium	Inorganic	Lung cancer
Cadmium	Inorganic	Lung ad prostate cancers
Chromium (VI)	Inorganic	Lung, nose and stomach cancers
4-Aminobiphenyl	Organic	Urinary-bladder cancer
1,2-Dichloropropane	Organic	Recently updated to Group 1; report in preparation
Ethylene oxide	Organic	Lympho-haematopoietic malignancies and breast cancer
Lindane	Organic	Recently updated to Group 1; report in preparation
Asbestos	Inorganic	Mesothelioma and lung cancer

This said, this doctoral thesis has a five-fold target:

- identifying critical local situations of exposure that are usually underrated by the environmental legislation and by the population;
- highlighting the critical aspects of the current environmental legislation and of the current approach towards the monitoring of air pollutants;
- proposing tools that allow for a deeper evaluation of the levels of exposure to air pollutants;
- proposing new or more precautionary limit values to preserve human health from unsafe exposure levels;
- providing options to optimize the design of specific emission sources or to purify the gaseous effluents prior to their final release into the atmosphere, taking into account the priority of carcinogenic organic pollutants.

However, also references to studies involving inorganic and non-carcinogenic pollutants will be cited in this doctoral thesis, especially when the intention is to focus on methodologies for the determination of critical situations of exposure and for the abatement of pollutants.

1.3 Outline

This research is composed of a total of five chapters. Each chapter contains extracts or references to works that are the results of this research activity. Most of them are published on peer-review journals, belonging to the ISI/SCOPUS circuit.

Hereinafter, this doctoral thesis will be organized according to the following structure:

- **Chapter 2: Critical situations of human exposure and current monitoring and regulatory approaches.** After an initial overview on underrated and uncontrolled situations of human exposure to air pollutants, this chapter summarizes the state of the art of exposure assessment methodologies and environmental monitoring techniques, with particular emphasis on the cancer risk assessment and the monitoring of carcinogenic compounds, like PCDD/Fs and benzene. Some limitations of the approaches towards the environmental monitoring and regulation of carcinogens will be also briefly reported. A significant part of the considerations is extracted from one publication produced during this research activity (Schiavon et al., 2016).
- **Chapter 3: Proposals for integrative methodologies for exposure assessment and environmental monitoring.** Four integrative methodologies for the exposure assessment and the environmental monitoring of air pollutants are presented, with a special focus on methods developed during this research activity, involving persistent organic pollutants (POPs) and benzene. The core results of works published during this research (Rada et al., 2013a, 2014a; Argiriadis et al., 2014; Schiavon et al., 2015a) will be presented.
- **Chapter 4: A proposal for a regulatory limit for atmospheric deposition of PCDD/Fs.** A regulatory limit for atmospheric deposition of PCDD/Fs to soil is proposed in this section, according to an

original formulation developed during this research (Schiavon et al., 2013). A reverse food-chain model was developed to directly obtain a tolerable PCDD/F deposition limit value based on the diet of a target population and moving from the PCDD/F tolerable daily intake suggested by the World Health Organization (WHO). The proposal for a limit value for atmospheric deposition of PCDD/Fs has the purpose of preserving the food chain, limiting human exposure and acting on the side of prevention at the receptor level.

- **Chapter 5: Proposals for improved design criteria for MBTs of solid waste.** This chapter presents strategies for the minimization of the impacts on human exposure at an emission level rather than at the receptor level. This chapter focuses on a critical analysis on the conventional technologies applied to treat streams contaminated by volatile organic compounds (VOCs) at low concentration, at the outlet of mechanical-biological treatments (MBTs) of solid waste. Specifically, critical considerations on conventional open biofilters are presented, especially in terms of dilution of the effluent released into the atmosphere. Such considerations drawn from two publications carried out during this research are presented (Ragazzi et al., 2014a; Schiavon et al., 2015b). Other biofiltration technologies, the so-called BTFs, are presented as an alternative and more effective solution. Their operation principles and their performance are discussed in a detailed review carried out during this research (Schiavon et al., 2015c).
- **Chapter 6: Proposals for enhanced emission control: Non-thermal plasmas.** This last chapter focuses on an innovative technology for air pollution control: non-thermal plasma. Two experimental studies, concerning the treatment of VOCs with non-thermal plasma are reported. Both these studies propose an enhanced method for the decontamination of VOC-polluted streams and, thus, for limiting human exposure by acting on the side of prevention at the emission level. The results of the first experience were published as a research paper during this doctoral activity (Schiavon et al., 2015d), while a paper on the results of the second experience was submitted to a journal.

2 Critical situations of human exposure and current monitoring and regulatory approaches

2.1 Summary

Anomalous situations of human exposure occur in different contexts (urban, rural or mountainous regions) and involve different groups of pollutants with different effects on health (acute or chronic, carcinogenic or non-carcinogenic). Besides well-known activities releasing amounts of air pollutants that may lead to critical concentrations in environmental media (*e.g.*, road traffic, chemical and petrochemical facilities, energy production plants from fossil fuels, etc.), there are several activities whose contribution to human exposure to air pollutants is underrated by the population and, in some situations, unregulated. Such activities may be responsible for underestimated pathways of human exposure. The first part of this chapter is dedicated to a short review of such situations. The second part focuses on two air pollutants: PCDD/Fs and benzene. Such substances are particularly important from the toxicological point of view, due to their high cancer potency. In addition, the lipophilicity of PCDD/Fs and the ubiquity of benzene may increase the potential exposure to these compounds and the associated cancer risk. An overview on the procedure of risk estimation will be presented, followed by critical aspects of the current monitoring approaches and new opportunities to improve conventional procedures.

2.2 Examples of underrated situations of human exposure

Various situations of the everyday life, sometimes considered as usual and harmless, are rather important sources of exposure to atmospheric pollutants. The air quality near gasoline stations was object of investigation in recent studies (Carrieri et al., 2006; Karakitsios et al., 2007a, 2007b; Morales Terrés et al., 2010). Benzene is the most frequent and toxic carcinogen present in fossil fuels. Fugitive emissions of benzene from petrol filling stations represent a potential risk both for the attendants and the people living in the surroundings. In order to quantify the level of the exposure to this pollutant, passive samplers were employed. As a result of one of these studies (Carrieri et al., 2006), gasoline station attendants are exposed to up to nine times the limit value for annual mean benzene concentration (5 $\mu g\ m^{-3}$). Higher concentrations were reported in Karakitsios et al.(2007a). The same authors quantified the area of influence of the gasoline station under investigation, which extends up to 100 m from the pumps. The European Parliament recently regulated the adoption of the Stage II Vapour Recovery System for specific categories of gasoline stations, which is expected to reduce the emissions of VOCs at least by 80% (European Union, 2009). Due to the recent introduction of such devices, no specific studies have been carried out to assess the efficacy of this solution on the exposure of attendants and resident population.

Benzene, but also nitrogen dioxide (NO_2), particulate matter (PM) and carbon monoxide (CO), are typical traffic-related pollutants. Due to the geometric configuration of the urban fabric, often characterized by narrow roads surrounded by continuous rows of buildings on both sides, the dispersion of pollutants into the atmosphere is limited. This is the case of the so-called urban street canyons, whose impact in terms of air quality was investigated in several studies (DePaul and Sheih, 1985; Kassomenos et al., 2004; Qin, 1993; Schiavon et al., 2014a; Tsai and Chen, 2004; Vardoulakis et al., 2005). Since street canyons promote the stagnation of air pollutants to the ground, due to the limited ventilation occurring inside, exposure to air pollutants is then sharpened within street canyons. In spite of this, the European legislation has not adopted environmental measures to keep urban street canyons under particular observation.

Potential situations of high exposure to air pollutants are likely to occur at the exit of road tunnels (Bari and Naser, 2010; Gouriou et al., 2004; Mak and Hung, 2008; Murena, 2007; Oettl et al., 2003). At these specific locations, the pollutants released inside tunnels are concentrated, since the entrance and the exit represent the only way out, except for some limited cases whereas aspiration fans convey the air of the tunnel to an exhaust chimney. In addition to the issues concerning the air quality in the surroundings of the tunnel exits, high levels of pollution are achieved inside tunnels (Svartengren et al., 2000). If recirculation systems for in-car ventilation are not activated by the driver and the ventilation fan is on, episodes of exposure to concentrations of NO_x, PM and CO exceeding the hourly and annual limit values are likely to occur (Chan and Chung, 2003; Svartengren et al., 2000). In general, short-term exposure to NO_2 and PM is particularly harmful for asthmatic people. Such conditions, as stated, can occur when transiting through highly polluted environments, like road tunnels. On the other hand, long-term exposure causes chronic pathologies. The exposure of residents living in the vicinity of tunnel exits belongs to this category. Hence, the residential population is subject to the possibility of contracting chronic diseases over the years. In-depth studies concerning the long-term exposure to air pollutants near road tunnels are still lacking in the literature, as a confirmation of the underestimation of this problem.

In addition to the emissions by gasoline stations and road traffic, where benzene is emitted mainly due to its presence in the fuel, this compound is also emitted by combustion processes through *de novo* formation: this is the case of wood combustion, which is usually characterized by heterogeneity of the temperature field inside the combustion chamber. This leads to incomplete oxidation of the gaseous organic compounds released by the fuel during the initial stage of combustion, which can react with radicals and generate benzene (IARC, 2010; Williams et al., 2012). Combustion processes are an important source of exposure to benzene, especially when such processes are routinely used by the population, *e.g.* for heating purposes. Wood burning is common both in developing and in developed countries. For instance, wood burning contributes to more than 50% of benzene emissions in the Scandinavian area. Similar contributions are expected in rural and mountainous regions where wood is largely available and used as source of energy. More and more efficient wood and pellet stoves have been introduced in the market over the last decades, with consequent improvements in the combustion process. However, recent studies highlighted the problem of indoor and outdoor air quality where biomass burning is commonly practiced (Gaeggeler et al., 2008; Gustafson et al., 2007; Hellén et al., 2008). Wood burning, as well as other combustion processes, is also responsible for emissions of PCDD/Fs. The latter are generated by thermal breakdown and rearrangement of chlorinated aromatic hydrocarbons, formed under conditions of incomplete combustion. *De novo* synthesis, by reaction with chlorine, oxygen, hydrogen and carbon, is also a possible mechanism of formation (Environment Australia, 1999).

In addition to the previously mentioned sectors, also waste treatments present some criticalities, since underestimated situations of exposure may occur as a consequence of specific processes. For instance, MBTs are considered an emerging option for waste treatment, usually depicted by the public opinion as more respectful for the environment and, sometimes erroneously, as an alternative to incineration. However, odours and toxic pollutants are released by this kind of processes (Höring et al., 1999). A recent study confirmed that the emission factor of PCDD/Fs from aerobic MBTs cannot be neglected (Rada et al., 2007). In addition, emissions from MBT plants are associated to low temperature and output speed of the flue gas, with negative consequences on the dilution of the plume within the atmosphere. The height of the emission point or surface (usually corresponding to the top of biofilters, located on the ground) is also a crucial factor for an efficient dispersion of pollutants. Although these criticalities, MBTs are not regulated by any European national legislation, except for Germany and Austria (Section 2.3.1.8). Due to the similarities with the biodrying process, biostabilisation may present the same issues in terms of emissive impact, as demonstrated in a recent study (Ragazzi et al., 2014a) presented at Section 5.2.

Indoor air pollution is an additional element of hidden risk. The perception of the level of exposure of the people may be very low when dealing with simple activities of the everyday life. Some practices, such as cooking activities, release high fluxes of PM and VOCs, leading to extremely high concentrations, especially if aspiration or ventilation systems are lacking, although such peaks are limited in time (Abdullahi et al., 2013; Y. Huang et al., 2011). However, acute exposure is a potential risk for asthmatic people and practicing cooking activities for a long time can potentially increase the cancer risk (Y. Huang et al., 2011). Except for occupational exposure, no environmental legislation covers the aspect of the daily life inside buildings and dwellings. Since people spend most of the time in indoor environments, the personal exposure to indoor air pollutants should be greatly taken into account.

2.3 PCDD/Fs and benzene: Widespread organic carcinogens

Among the organic carcinogenic compounds, PCDD/Fs and benzene are ubiquitous pollutants that can potentially affect large groups of individuals. Due to their lipophilic properties, PCDD/Fs are able to enter the food chain and finally accumulate in the human body. Benzene is particularly present in urban areas, which are generally characterized by high population density; hence, the exposure to benzene can potentially involve a large number of inhabitants.

2.3.1 PCDD/Fs

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2.3.1.1 Introduction

PCDD/Fs and PCBs are semi-volatile chlorinated organic compounds, which are lipophilic, hydrophobic and chemically stable (Lee and Nicholson, 1994). These characteristics lead to a strong resistance to environmental degradation, which causes the tendency to magnification in the food chain and bioaccumulation in animal and human tissues. Their low solubility in water even decreases with increasing the degree of chlorination (Mackay et al., 2006). For these reasons, PCDD/Fs and PCBs are classified as POPs.

PCDD/Fs are composed of 75 PCDD and 135 PCDF congeners. Among these, 17 congeners (7 for PCDDs and 10 for PCDFs) are particularly harmful to humans (IARC, 2015a). Their toxicity depends on the number and position of the chlorine atoms on the aromatic ring. The most toxic compounds are the 2,3,7,8-tethrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and the 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (1,2,3,7,8-PeCDD) (Van den Berg et al., 2006). Among the 209 congeners that compose the group of PCBs, 12 coplanar congeners demonstrated toxic effects similar to those provoked by the 17 PCDD/F toxic congeners. For this reason, such compounds are usually referred to as “dioxin-like PCBs” (WHO, 2014).

Several studies report that more than 90% of the daily intake of PCDD/Fs results from ingestion of contaminated food (Eduljee and Gair, 1996; Sasamoto et al., 2006). Thus, if specific situations of direct exposure by inhalation are excluded (Morra et al., 2006), the food chain is the primary pathway of exposure. PCDD/Fs, mainly emitted into the atmosphere, are partially adsorbed to PM, which reaches the soil and the vegetation through atmospheric deposition; PCDD/Fs can then contaminate cultivations (*e.g.*, cereals and, less commonly, vegetables) and grass; hence, PCDD/Fs can directly enter the human body at this stage, through consumption of contaminated cereals and vegetables, or can contaminate the diet of cattle and livestock in general, through grass consumption and accidental soil ingestion; therefore, humans are exposed to PCDD/F intake by consumption of contaminated meat, eggs, fish, milk and dairy products. The higher contribution from one kind of food rather than another depends on the diet of the single individual, although cereals, meat, fish, milk and dairy products are major contributors (Fattore et al., 2006; De Mul et al., 2008; Bilau et al., 2009). Minor contributions are given by inhalation of contaminated air, accidental ingestion of soil and dermal contact.

PCDD/Fs are not industrial products, but are unwanted sub-products of thermal reactions or incomplete combustion in the presence of precursors containing chlorine (Fiedler, 1996). In thermal processes, between 500 and 800 °C, PCDD/Fs are formed in the gas phase by pyrolytic rearrangement of precursors (*e.g.*, chlorophenols and chlorobenzenes) (Stanmore, 2004). As an alternative, at lower temperatures (200-400 °C), PCDD/Fs may undergo *de novo* formation, through oxidation of existing polycyclic compounds and subsequent chlorination, mediated by catalysts. Chlorine is usually made available in solid phase by chlorinated compounds or is present as atomic chlorine (Stanmore, 2004). During the last twenty years, different kinds of improvements have been introduced in the processes responsible for the generation of PCDD/Fs and in the technologies for air pollution control (APC). However, some situations are still uncontrolled and their contribution to releases of POPs may be underrated. On the other hand, a complete and detailed monitoring of all the pathways of exposure to PCDD/Fs and PCBs is technically and economically unfeasible.

2.3.1.2 Effects on human health

2,3,7,8-TCDD is the most studied congener, since it is an endocrine disruptor and a demonstrated carcinogen for humans, classified by the International Agency for Research of Cancer (IARC) in the Group 1 (IARC, 2015a). The remaining 6 toxic PCDD congeners are classified by the IARC as belonging to the Group 3, showing inadequate evidence of carcinogenicity in humans. The 12 dioxin-like PCBs were recently upgraded from Group 2A to Group 1, due to strong supporting evidence to their cancer potential, as well as all the 10 PCDF toxic congeners (IARC, 2015a).

Short-term (or acute) exposure to high concentrations of 2,3,7,8-TCDD alters the liver function and may cause skin lesions, like persistent chloracne and patchy darkening of the skin (WHO, 2014). Long-term (or chronic) exposure to 2,3,7,8-TCDD may result also in carcinogenic effects, such as lung cancer, soft-tissue sarcoma, non-Hodgkin lymphoma, digestive system cancer, multiple myeloma and other malignant neoplasms (IARC, 1997).

The main mechanism of interaction between the 29 congeners and a living system involves the activation of the aryl hydrocarbon receptor (AhR), which is a transcription factor gene (Beischlag et al., 2008). Thus, PCDD/Fs are not directly genotoxic: the cancer promotion is mediated by a chain starting with the alteration of the AhR and subsequent damage to DNA (IARC, 1997). 2,3,7,8-TCDD has the strongest affinity with AhR, which may explain the higher toxicity of this congener.

2.3.1.3 Determination of toxicity

The toxicity equivalence factor (TEF) is a parameter that defines the estimated toxicity of each congener with respect to an index chemical (US EPA, 2010). With regards to dioxin-like compounds, the index chemical is 2,3,7,8-TCDD (Van den Berg et al., 1998). The main assumption behind the TEF definition is that the effects of each congener are dose or concentration additive (Van den Berg et al. 1998). The weighted toxicity of each “*i*” congener, expressed as toxic equivalency (TEQ_i), is obtained by multiplying the concentration of the chemical by its TEF. The overall toxicity of a mixture (TEQ) is expressed by summing up the contribution of each congener. The WHO suggested to re-evaluate TEFs about every five years and update them on the basis of new scientific information (US EPA, 2010).

Prior to the TEF definition schemes proposed by the WHO, other schemes were provided by the United States Environmental Protection Agency (US EPA) and the North Atlantic Treaty Organization (NATO). The latter is commonly referred to as International TEF (I-TEF) scheme. The evolution in the definition of the main TEF schemes is summarized in Table 2.1.

Table 2.1: Evolution of the TEFs of PCDD/Fs and dioxin-like PCBs.

		US-EPA 1987[a]	**NATO 1989**[b]	**WHO 1994**[c]	**WHO 1998**[d]	**WHO 2005**[e]
PCDDs						
2,3,7,8-TCDD		1	1		1	1
1,2,3,7,8-PeCDD		0.5	0.5		1	1
1,2,3,4,7,8-HxCDD		0.04	0.1		0.1	0.1
1,2,3,6,7,8-HxCDD		0.04	0.1		0.1	0.1
1,2,3,7,8,9-HxCDD		0.04	0.1		0.1	0.1
1,2,3,4,6,7,8-HpCDD		0.001	0.1		0.01	0.01
1,2,3,4,6,7,8,9-OCDD		0	0.001		0.0001	0.0003
PCDFs						
2,3,7,8-TCDF		0.1	0.1		0.1	0.1
1,2,3,7,8-PeCDF		0.1	0.05		0.05	0.03
2,3,4,7,8-PeCDF		0.1	0.5		0.5	0.3
1,2,3,4,7,8-HxCDF		0.01	0.1		0.1	0.1
1,2,3,6,7,8-HxCDF		0.01	0.1		0.1	0.1
2,3,4,6,7,8-HxCDF		0.01	0.1		0.1	0.1
1,2,3,7,8,9-HxCDF		0.01	0.1		0.1	0.1
1,2,3,4,6,7,8-HpCDF		0.001	0.1		0.01	0.01
1,2,3,4,7,8,9-HpCDF		0.001	0.1		0.01	0.01
1,2,3,4,6,7,8,9-OCDF		0	0.001		0.0001	0.0003
dioxin-like PCBs						
3,3’,4,4’-TCB	(PCB 77)			0.0005	0.0001	0.0001
3,4,4’,5-TCB	(PCB 81)			-	0.0001	0.0003
2,3,3’,4,4’-PeCB	(PCB 105)			0.0001	0.0001	0.00003
2,3,4,4’,5-PeCB	(PCB 114)			0.0005	0.0005	0.00003
2,3’,4,4’,5-PeCB	(PCB 118)			0.0001	0.0001	0.00003
2’,3,4,4’,5-PeCB	(PCB 123)			0.0001	0.0001	0.00003
3,3’,4,4’,5-PeCB	(PCB 126)			0.1	0.1	0.1
2,3,3’,4,4’,5-HxCB	(PCB 156)			00005	00005	0.00003
2,3,3’,4,4’,5’-HxCB	(PCB 157)			0.0005	0.0005	0.00003
2,3',4,4',5,5'-HxCB	(PCB 167)			0.00001	0.00001	0.00003
3,3',4,4',5,5'-HxCB	(PCB 169)			0.01	0.01	0.03
2,3,3',4,4',5,5'-HpCB	(PCB 189)			0.001	0.001	0.00003

[a] US EPA (1997)
[b] NATO/CCMS (1988)
[c] Ahlborg et al. (1994)
[d] Van den Berg et al. (1998)
[e] Van den Berg et al. (2006)

2.3.1.4 Risk Estimation and related parameters

In this section, priority is given to long-term exposure and to chronic effects on health, which are usually hidden due to the low levels of concentrations that characterize this type of exposure.

2.3.1.4.1 Non-carcinogenic effects

The parameters that allow estimating the non-cancer risk are the US EPA’s reference dose (*RfD*) or the reference concentration (*RfC*), depending on the route of exposure (oral or inhalation, respectively). *RfD* (or *RfC*) is defined as the daily dose (or mean concentration) of a specific substance that is likely to avoid an appreciable risk of adverse effects during a lifetime (US EPA, 2015a). The *RfD* is expressed in mg of substance per kg of body weight per day (mg kg^{-1} d^{-1}), whilst the *RfC* is expressed as mg m^{-3} of air contaminant.

The tolerable daily intake (TDI), was proposed by the WHO in 1990 for exposure by ingestion (WHO, 1991). The TDI was introduced to ensure a level of exposure that should not lead to an appreciable health risk over a lifetime (WHO, 2008). The TDI for PCDD/Fs and dioxin-like PCBs was progressively refined over the years: the first formulation, proposed by the WHO, defined a value of 10 pg WHO-TEQ kg^{-1} of body weight per day (WHO, 1991); in 1998 the WHO updated this value to a range of 1-4 pg WHO-TEQ kg^{-1} d^{-1}, stressing the necessity of reaching a final value of 1 pg WHO-TEQ kg^{-1} d^{-1} (WHO, 1998). The current guide value proposed by the European Community is 14 pg WHO-TEQ kg^{-1} per week (European Commission, 2006a).

2.3.1.4.2 Carcinogenic effects

The US EPA's approach towards carcinogenic effects assumes a linear dose-response relationship with no threshold, since a damage to a single cell can be sufficient to cause cancer. The slope of this curve, called "cancer potency" or "slope factor" (SF), defines the cancer risk at low doses, expressed in probabilistic terms (US EPA, 2005a). Substance-specific SFs have been proposed by the US EPA both for ingestion (SF_{oral}) and for inhalation (SF_{inhal}). SFs are expressed in terms of (mg kg^{-1} d^{-1})$^{-1}$. A simplification of the concept of SF is given by the introduction of the unit risk (UR) approach: the UR expresses the cancer potency in terms of concentration of a substance in water or in air (US EPA, 2005a). Exposure occurs through ingestion (UR_{oral}) in the first case and through inhalation (UR_{inhal}) in the second case. The UR is defined as the upper-bound excess lifetime risk of cancer that can derive from continuous exposure to 1 µg L^{-1} or 1 µg m^{-3} of a carcinogenic substance, in water or in air, respectively (US EPA, 2015a). Similarly to *RfC*, the UR combines information on the exposure with information on the toxicity of an agent (Benjamin and Belluck, 2001). The UR is expressed in terms of (µg L^{-1})$^{-1}$ or (µg m^{-3})$^{-1}$, for water ingestion or inhalation, respectively.

Congener-specific values for *RfD* and cancer-risk parameters (SF_{oral}, SF_{inhal} and UR_{inhal}) are provided by the US EPA and are reported in Table 2.2. No congener-specific values for UR_{oral} are provided for dioxin and dioxin-like compounds. A general value of 1.0E-05 (µg L^{-1})$^{-1}$ is proposed for PCBs. SFs for non-dioxin-like PCBs are also provided by the US EPA concerning the inhalation and ingestion routes, both equal to 2 (mg kg^{-1} d^{-1})$^{-1}$ (US EPA, 2012). Since also non-dioxin-like PCBs can cause cancer, their total dose should be multiplied by the generic PCB SF and the consequent risk should be added to that induced by dioxin-like PCBs (US EPA, 2000).

2.3.1.4.3 Cancer risk calculation

The cancer risk (*R*) is finally estimated by multiplying the suitable parameter (SF_{oral}, SF_{inhal}, UR_{oral} or UR_{inhal}) by exposure (this applies only to SF_{oral} and SF_{inhal}) and by the average concentration of the substance in the environmental medium (Benjamin and Belluck, 2001):

$$R = C \cdot E \cdot SF = C \cdot UR \qquad \text{Eq. 2.1}$$

where C is the average concentration in the medium (expressed in mg kg^{-1}, µg L^{-1} or µg m^{-3}, according as the exposure occurs by food ingestion, water ingestion or inhalation, respectively) and E is the exposure.

The use of the SF approach requires knowledge of more detailed parameters, since E is defined as follows:

$$E = \frac{IR \cdot ED \cdot EF}{BW \cdot AT} \qquad \text{Eq. 2.2}$$

where IR is the intake rate of medium (expressed in mg d^{-1}, L d^{-1} or m^3 d^{-1}, according as the exposure occurs by food ingestion, water ingestion or inhalation, respectively); if referring to inhalation, IR is about 16 m^3 d^{-1} of air for adults (Stifelman, 2007), even though the US EPA proposes a more precautionary value of 20 m^3 d^{-1} (US EPA, 2005a); if referring to water consumption, IR can be assumed as 2 L d^{-1} for adults and 1 L d^{-1} for children (US EPA, 2005a); ED is the exposure duration (expressed in y); EF is the exposure frequency (expressed in d y^{-1}); BW is the body weight (expressed in kg); AT is the averaging time (expressed in y), normally assumed as 70 y (US EPA, 2005a). To account for the amplification of the risk related to the exposure oc-

Table 2.2: Congener-specific values for RfD, SF_{oral}, SF_{inhal} and UR_{inhal}.

		RfD **[mg kg^{-1} d^{-1}]**	**SF_{oral}** **[(mg kg^{-1} $d^{-1})^{-1}$]**	**SF_{inhal}** **[(mg kg^{-1} $d^{-1})^{-1}$]**	**UR_{inhal}** **[(µg $m^{-3})^{-1}$]**
PCDDs[a]					
2,3,7,8-TCDD		7.0E-10	1.3E+05	1.3E+05	3.8E+01
1,2,3,7,8-PeCDD		7.0E-10	1.3E+05	1.3E+05	3.8E+01
1,2,3,4,7,8-HxCDD		7.0E-11	1.3E+04	1.3E+04	3.8E+00
1,2,3,6,7,8-HxCDD		7.0E-11	6.2E+03	4.5E+03	1.3E+00
1,2,3,7,8,9-HxCDD		7.0E-11	6.2E+03	4.5E+03	1.3E+00
1,2,3,4,6,7,8-HpCDD		7.0E-12	1.3E+03	1.3E+03	3.8E-01
1,2,3,4,6,7,8,9-OCDD		2.0E-13	3.9E+01	3.8E+01	1.1E-02
PCDFs[a]					
2,3,7,8-TCDF		7.0E-11	1.3E+03	1.3E+04	3.8E+00
1,2,3,7,8-PeCDF		2.0E-11	3.9E+03	3.8E+03	1.1E+00
2,3,4,7,8-PeCDF		2.0E-10	3.9E+04	3.8E+04	1.1E+01
1,2,3,4,7,8-HxCDF		7.0E-11	1.3E+04	1.3E+04	3.8E+00
1,2,3,6,7,8-HxCDF		7.0E-11	1.3E+04	1.3E+04	3.8E+00
2,3,4,6,7,8-HxCDF		7.0E-11	1.3E+04	1.3E+04	3.8E+00
1,2,3,7,8,9-HxCDF		7.0E-11	1.3E+04	1.3E+04	3.8E+00
1,2,3,4,6,7,8-HpCDF		7.0E-12	1.3E+03	1.3E+03	3.8E-01
1,2,3,4,7,8,9-HpCDF		7.0E-12	1.3E+03	1.3E+03	3.8E-01
1,2,3,4,6,7,8,9-OCDF		2.0E-13	3.9E+01	3.8E+01	1.1E-02
PCBs[b]					
3,3’,4,4’-TCB	(PCB 77)	-	1.3E+01	3.8E-03	1.3E+01
3,4,4’,5-TCB	(PCB 81)	-	1.3E+01	3.8E-03	1.3E+01
2,3,3’,4,4’-PeCB	(PCB 105)	-	1.3E+01	3.8E-03	1.3E+01
2,3,4,4’,5-PeCB	(PCB 114)	-	6.5E+02	1.9E-02	6.5E+02
2,3’,4,4’,5-PeCB	(PCB 118)	-	1.3E+01	3.8E-03	1.3E+01
2’,3,4,4’,5-PeCB	(PCB 123)	-	1.3E+01	3.8E-03	1.3E+01
3,3’,4,4’,5-PeCB	(PCB 126)	-	1.3E+04	3.8E-00	1.3E+04
2,3,3’,4,4’,5-HxCB	(PCB 156)	-	6.5E+01	1.9E-02	6.5E+01
2,3,3’,4,4’,5’-HxCB	(PCB 157)	-	6.5E+01	1.9E-02	6.5E+01
2,3',4,4',5,5'-HxCB	(PCB 167)	-	1.3E+00	1.3E+00	3.8E-04
3,3',4,4',5,5'-HxCB	(PCB 169)	-	1.3E+03	1.3E+03	3.8E-01
2,3,3',4,4',5,5'-HpCB	(PCB 189)	-	1.3E+01	3.8E-03	1.3E+01

[a] US EPA (2014)
[b] OEHHA (2009)

curring in the early-life stages, age-dependent adjustment factors (ADAFs) can be introduced for each period of life ($ADAF$=10 for age < 2 y; $ADAF$=3 for 2 y ≤ age < 16 y; $ADAF$=1 for age ≥ 16 y). For each "*i*" period, the risk results in (US EPA, 2005a):

$$R = C \cdot \frac{IR \cdot ED \cdot EF}{BW \cdot AT} \cdot ADAF \cdot SF \qquad \text{Eq. 2.3}$$

The total cancer risk is obtained by sum of the single n contributions (with $1 \leq n \leq 3$):

$$R = \sum_{i=1}^{n} R_i \qquad \text{Eq. 2.4}$$

The overall cancer risk is assumed to be given by the sum of the cancer risks (related to the same target organ) induced by each substance and through each route of exposure.

Due to the absence of a threshold dose for carcinogenic contaminants, the cancer risk is never zero, but may be enough low to be considered acceptable. Conventionally, the cancer risk is considered acceptable if comprised between 10^{-6} and 10^{-4}, *i.e.*, if it is able to induce no more than 1 excess case of cancer in 1,000,000 to 10,000 inhabitants (US EPA, 1999a). A risk lower than 10^{-6} is normally considered as the optimal risk level, even though values up to 10^{-4} are tolerated. The choice of the target value can depend on the population density of an area or on the economic feasibility of the efforts requested to reduce the impacts (US EPA, 1999a). On the other hand, the concept of "acceptable risk" was clarified and inserted in a regulation by the Italian legislation: the acceptable excess cancer risk is 10^{-6} in the case of exposure to a single compound and 10^{-5} in the case of exposure to a group of compounds (Italian Republic, 2008).

2.3.1.5 Atmospheric fate

When emitted into the atmosphere, PCDD/Fs and PCBs in the gas phase are mainly subject to photolysis and reaction with ozone (O_3), nitrate (NO_3) radical and, especially, hydroxyl (·OH) radicals (Atkinson, 1996; Lohmann and Jones, 1998). The photodegradation rate decreases when the degree of chlorination increases (Wu et al., 2005). Catalytic conversion, atmospheric transport and, finally, deposition represent the main routes for particle-bound congeners (Atkinson, 1996). Lowly-chlorinated congeners are associated with larger particles (> 2.1 µm), whilst highly-chlorinated congeners are often associated with fine particles (< 2.1 µm) (Oh et al., 2002): this lets suppose that lowly-chlorinated congeners may not be transported at great distance from the source. Thus, their local impact may be higher with respect to congeners with higher degree of chlorination. Furthermore, the toxicity of lowly-chlorinated congeners is higher, especially with regards to PCDD/Fs.

Higher concentration levels of PCDD/Fs and PCBs are normally observed in winter with respect to summer, both because of the lower height of the atmospheric boundary layer and because additional emission sources (*e.g.*, domestic heating) are present in winter (Ding et al., 2012). After their emission into the atmosphere, the lower chlorinated compounds show higher tendency to remain in the gas phase; as the degree of chlorination grows, the affinity to the particle phase increases (Lohmann and Jones, 1998). This behaviour seems to be correlated with the octanol-air partition coefficient of each congener (Lohmann et al., 2007) and with their vapour pressure (Saral et al., 2015). Temperature also influences the partitioning: low temperatures contribute to a higher particle-phase fraction (Lee et al., 2008), thus a seasonality can be observed during the year (Ding et al., 2012; Saral et al., 2015).

2.3.1.6 Limit and guideline values in environmental media

In Europe, waste incinerators are obliged to comply with a concentration of 0.1 ng I-TEQ Nm^{-3} at the stack (European Union, 2000). The concentration of PCDD/Fs and dioxin-like compounds in foodstuffs is also regulated: at a European level, for instance, limit values for PCDD/Fs and dioxin-like PCBs in foodstuffs were firstly introduced in 2001 (European Commission, 2001) and then re-evaluated twice in 2006 (European Commission, 2006a, 2006b). In the last formulation (European Commission, 2011), maximal PCDD/F and dioxin-like PCB concentrations are reported for different types of food.

Only guide values, with no regulatory purpose, were introduced for ambient air and sediment concentrations, and for atmospheric deposition. Limit values on soil concentrations exist in some countries: in Italy, for instance, PCDD/F limit values of 10 ng WHO-TEQ kg^{-1} on dry weight (dw) for residential and green areas and 100 ng WHO-TEQ kg^{-1}_{dw} for commercial and industrial areas have been in force since 2006 (Italian Republic, 2006). The same decree sets limit values for PCBs to 0.06 mg kg^{-1}_{dw} and 5 mg kg^{-1}_{dw} for residential and green areas and for commercial and industrial areas, respectively (Italian Republic, 2006).

The absence of regulatory prescriptions is of particular concern for atmospheric deposition, if considering the lipophilic behaviour of POPs and their capability to accumulate in the food chain.

2.3.1.7 Typical levels in the environment

The ambient air concentration gradually increases when moving from rural areas to urban and industrial districts (Abad et al., 2007). Concentrations in the range 5-45 fg I-TEQ m^{-3}, 10-357 fg I-TEQ m^{-3} and 5-1196 fg I-TEQ m^{-3} were measured in Catalonia (Spain) during a ten-year study (1994-2004) in rural, urban and industrial areas, respectively (Abad et al., 2007). Concentrations measured near a municipal solid waste (MSW) incinerator in Italy were comprised between 22 and 337 fg I-TEQ m^{-3} (Caserini et al., 2004). Concentrations between 10 and 138 fg I-TEQ m^{-3} were measured in the urban area of Trento (Italy) in 2006-2007 (Ragazzi et al., 2014a); monitoring campaigns carried out in other cities showed mean concentrations of 40-119 fg I-TEQ m^{-3} in Thessaloniki (Greece) (Kouimtzis et al., 2002), 26-220 fg I-TEQ m^{-3} in Manchester (Lohmann et al., 2000), 65 fg I-TEQ m^{-3} in Rome (Menichini et al., 2007) and 40-55 fg I-TEQ m^{-3} in Houston (Correa et al., 2004). Concentration levels are higher in developing countries: in China, for instance, mean PCDD/F concentrations of 57-1280 fg I-TEQ m^{-3} were measured in Guangzhou (Yu et al., 2006) and 18-644 fg I-TEQ m^{-3} in Beijing (Li et al., 2008), whilst concentrations of 156-1440 fg I-TEQ m^{-3} were measured near an MSW incinerator (Zhang et al., 2014).

Atmospheric deposition of PCDD/Fs varying from 0.75 pg WHO-TEQ m^{-2} d^{-1} to 3.73 pg WHO-TEQ m^{-2} d^{-1} were measured in the surroundings of an MSW incinerator in Italy (Vassura et al., 2011). In an Italian valley, characterized by the presence of a steel plant equipped with the best available technologies (BATs), the mean PCDD/F deposition measured during one year was 1.40 pg WHO-TEQ m^{-2} d^{-1} (Schiavon et al., 2013). In a similar context, in the vicinity of an Italian steel plant, the PCDD/F deposition measured during one year resulted in the range 0.91-3.17 pg I-TEQ m^{-2} d^{-1} (Onofrio et al., 2011).

Concentrations in soil are also variable depending on the land use: industrial areas in Slovakia showed PCDD/F soil concentrations of 2.74-7.80 ng WHO-TEQ kg^{-1}_{dw}, whilst a concentration of 0.66 ng WHO-TEQ kg^{-1}_{dw} was measured at a background site (Dömötörová et al., 2012). A monitoring campaign carried out in the Alpine valley of Trento (Italy) showed mean values ranging from 0.14 ng I-TEQ kg^{-1}_{dw} (background site) and 4.86 ng I-TEQ kg^{-1}_{dw} (industrial site), with intermediate values of 0.92-0.96 ng I-TEQ kg^{-1}_{dw} observed along a highway (Rada et al., 2015).

The emissions of PCDD/Fs and dioxin-like PCBs have generally decreased during the last twenty years, especially due to improvements in the industrial sector and after the adoption of the BATs (Argiriadis et al., 2014). Monitoring campaigns carried out in an urbanized valley in Italy showed a continuous decrease in the ambient air concentrations of urban background areas, from 110.4 fg I-TEQ m^{-3} in 2002 to 17.38-24.45 fg I-TEQ m^{-3} in 2009-2010 (Ragazzi et al., 2014b). A 70% decline was observed between 1994 and 2004, during the monitoring campaign in Catalonia (Rada et al., 2015). The atmospheric deposition of PCDD/Fs and PCBs decreased from 12-32 pg I-TEQ m^{-2} d^{-1} to 5-10 pg I-TEQ m^{-2} d^{-1} between 1992 and 2011 in the Rhine-Ruhr region (Bruckmann et al., 2013). PCDD/F soil concentrations near a steel plant in an Alpine valley decreased from 4.10 ng I-TEQ kg^{-1} in 2010 to 2.14 ng I-TEQ kg^{-1} in 2012 (Rada et al., 2015).

In spite of their general reduction, critical PCDD/F and PCB levels are still observed near industrial facilities, especially in developing countries: very high concentrations in soil can be observed near abandoned industrial areas, like in the case of a pentachlorophenol factory in China, where average PCDD/F concentrations of 193 ng WHO-TEQ kg^{-1} and 667 ng WHO-TEQ kg^{-1} were measured in soil and sediment samples, respectively (Li et al., 2012); in the vicinity of another Chinese pentachlorophenol factory, the average PCDD/F air concentration was 39.7 pg I-TEQ m^{-3} (Chang et al., 2011).

Given the dominant role of the food chain in the exposure to PCDD/Fs and PCBs, atmospheric deposition should be regarded with particular attention. Contrarily to ambient air concentrations, there is a lower number of monitoring activities concerning deposition fluxes. The introduction of limit values for PCDD/Fs and PCBs in food (European Commission, 2006a) is a strategy to reduce human exposure through consumption of industrial products, but may not be sufficient to limit the intake to the target value of 1 pg WHO-TEQ kg^{-1} d^{-1}, as it actually occurs in various countries (Fattore et al., 2006). Furthermore, limit values for the PCDD/F and PCB content in foodstuffs may not preserve the population from the intake related to the consumption of locally-produced food (Heimstad et al., 2015).

2.3.1.8 Traditional and emerging emission sources

The presence of PCDD/Fs was historically associated to large-scale thermal processes, such as waste incineration, cement kilns, wood and coal burning for energy production, road traffic, non-ferrous metal smelting and production of iron and steel (Schecter et al., 1995; Fiedler, 1996; Stanmore, 2004). During the last decade, important improvements have been introduced in the technologies for APC. Positive results have been achieved in the emissions from road traffic (Shields et al., 2014). In addition, the combination of improved conditions of combustion, the adoption of the BATs and the imposition of strict emission limits have led to considerably reduce the impacts of MSW incinerators (Schecter et al., 1995; Ragazzi et al., 2013a).

The reduction of the emissions from these processes let other sectors become important sources of PCDD/Fs, such as residential wood burning. According to the last comprehensive inventory on PCDD/F emission in Europe (Quaß et al., 2004), residential wood burning is the highest contributor of PCDD/Fs in the environment with 523-969 g I-TEQ y^{-1}. This sector is followed by sintering plants (387-470 g I-TEQ y^{-1}), preservation of wood (118-310 g I-TEQ y^{-1}), fires (60-371 g I-TEQ y^{-1}), residential coal burning (82-337 g I-TEQ y^{-1}), MSW incineration (178-232 g I-TEQ y^{-1}) , steel plants equipped with electric-arc furnace (141-172 g I-TEQ y^{-1}) and domestic waste burning (116-187 g I-TEQ y^{-1}) (Quaß et al., 2004). This ranking may slightly change, depending on the study area, as demonstrated in a recent publication on Portugal, where the main contributing sector is forest fires, followed by wood preservation and domestic wood burning (Relvas et al., 2013).

Thanks to researches carried out in the last decade, a new sector has been identified as a potential non-negligible emitter of PCDD/Fs: MBTs of MSW, such as composting, biostabilisation and biodrying (Rada et al., 2006). Differently from thermo-chemical processes, PCDD/Fs are not produced in MBTs, but can be released since such compounds can be present in traces in the incoming waste (Rada et al., 2006). PCDD/Fs can be partially stripped by the process air, which becomes enriched in PCDD/Fs and releases them at the outlet (Liu et al., 2009). There is great variability in the emission factors reported in the literature, since PCDD/F emissions depend on the APC strategies adopted and on the PCDD/F content in the waste, specifically in the food waste, variable country by country (Ionescu et al., 2012).

At a European level, only Germany and Austria set PCDD/F concentration limit values for the emissions from MBTs. The limit is equal to that of MSW incinerators (0.1 ng I-TEQ Nm^{-3}) (BMLFUW, 2002; BMU, 2001). However, considering MSW incineration and MBTs at the same level can lead to erroneous considerations: indeed, potentially high impacts are expected in the surroundings of a MBT plant if the dispersion in the atmosphere is not optimized[1]. The conventional APC systems adopted in MBTs are based on biofiltration, especially open biofilters. The latter are located at ground level and are characterized by low velocities of the outgoing treated airstream (in the order of cm s^{-1}). Such conditions negatively affect the dilution of the plume in the atmosphere (Rada et al., 2011; Ragazzi et al., 2014a; Schiavon et al., 2015b).

2.3.1.9 Conventional methodologies for environmental monitoring and exposure assessment

The human exposure and the health risk associated with emissions of toxic and persistent pollutants could be directly determined if the human habits of the single individual and the contamination levels in all the major environmental media were known. In this case, the contaminants should be continuously monitored at a single-individual level. In the case of POPs, if considering that oral exposure is dominant with respect to inhalation, the main object of the monitoring activity should be the food. Nevertheless, analyses on food (other than the regulatory inspections) would require time and high costs. Thus, the most convenient approach con-

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[1] Such consideration will be demonstrated at Chapter 5.5

sists in the measurement of ambient air concentrations and atmospheric deposition to soil or in the analysis on the sediments of water basins.

2.3.1.9.1 *Ambient air concentration*

The most common methodology adopted to sample air for PCDD/F and PCB determination is based on the use of passive samplers and, specifically, on the US EPA TO-9A method (Castro-Jiménez et al., 2012; Ragazzi et al., 2014b), consisting in the use of a high-volume air sampler equipped with a quartz-fibre filter and a polyurethane foam adsorbent to trap the gaseous phase (US EPA, 1999). Active sampling, following the same prescriptions for PM, can be also performed (Cortés et al., 2014). The analyses are usually carried out with gas chromatography (GC) and high-resolution mass spectrometry (HRMS) after extraction of the sample with a mixture of acetone and exhane. However, in spite of a higher accuracy, such method implies higher costs for instrumentation and maintenance compared with passive sampling; higher costs may translate in a lower number of sampling points and this would decrease the spatial resolution of the monitoring network; as a consequence, possible local situations of critical exposure might not be observed with this methodology.

2.3.1.9.2 *Atmospheric deposition*

Atmospheric deposition occurs through removal processes that take place in dry or wet conditions. The dry deposition, active in the absence of precipitation, deposits the pollutants on the surface of soil or vegetation by the combined action of turbulent diffusion, gravitational sedimentation and inertial impaction. The wet deposition occurs in the presence of precipitation, through processes of incorporation of the pollutants in the clouds ("rainout") and run-off pollution ("washout"). While in dry conditions the pollutants are deposited mainly in the vicinity of the emission source, in wet conditions the pollutants can be transported over long distances (U.S. Government, 1984).

The dry deposition (D_d) is related to the ambient air concentrations of the pollutants in gas phase ($C_{a,g}$) and in particle phase ($C_{a,p}$) through the respective deposition velocities (V_{dg} and V_p):

$$D_d = C_a V_d = C_{a,g} V_{dg} + C_{a,p} V_p \qquad \text{Eq. 2.5}$$

where V_d is the total dry deposition velocity and C_a is the total air concentration (Lin et al., 2010). A mean value of 0.42 cm s^{-1} was provided for V_d by Shih et al. (2009), while a value of 0.010 cm s^{-1} was provided for V_{dg} by Sheu et al. (1996). A mean value of 0.44 cm s^{-1} for V_p was obtained by Lin et al. (2010). For diameters greater than the 10-20 µm, the speed is substantially coincident with that obtainable using the Stokes law, while, for the finest particles (< 0.2-0.5 µm), the Brownian motion becomes more significant. For intermediate sizes (0.5-5 µm) the combined intervention of the two mechanisms is likely to determine the minimum speed.

The wet deposition is composed by the contribution of the suspended particles removed by the precipitation and by the dissolution of the contaminant at the vapour phase. The wet deposition (D_w) is defined as:

$$D_w = C_a \cdot S_{tot} \cdot h_p \qquad \text{Eq. 2.6}$$

where h_p is the precipitation rate and S_{tot} is the total scavenging ratio, representing the ratio between the concentration in the liquid phase produced by the precipitation and the concentration in air at ground level. S_{tot} is the sum of the contribution deriving from the concentration of the particle-bound contaminant in the raindrop (S_p) and the concentration of the contaminant in the dissolved phase in the raindrop (S_g) (Lin et al., 2010):

$$S_{tot} = S_p \Phi + S_g (1 - \Phi) = \Phi \frac{C_{r,p}}{C_{a,p}} + (1 - \Phi) \frac{C_{r,g}}{C_{a,g}} \qquad \text{Eq. 2.7}$$

where $C_{r,p}$ is the particle-phase concentration in the raindrop, $C_{r,g}$ is the dissolved-phase concentration in the raindrop and Φ is the ratio between the air concentration of contaminant bound to particles and the total air concentration (Lin et al., 2010).

The traditional methodology to monitor the bulk (wet and dry) deposition of organic compounds, still adopted in the deposition monitoring, follows the indications of the Bergerhoff® method (VDI, 1996), consisting in a glass-made funnel-jar collection system, protected by a cylindrical container and a ring to avoid interferences by bird excreta (Guerzoni et al., 2004). Wet and dry deposition can be separately measured by adopting a double deposition sampling system equipped with a moveable cover, which can be automatically activated by a rain or moisture sensor (Anderson and Downing, 2006). The standard analytical methods to obtain the deposition of PCDD/Fs and PCBs are the US EPA Method 1613 (US EPA, 1994) and the US EPA Method 1668B (US EPA, 2008). If air sampling is the most direct method to assess exposure through inhalation, deposition sampling represents a low-cost alternative with respect to analyses on food if the target is the assessment of exposure through ingestion; this is due to the possibility of coupling deposition measurements with food chain models and statistics on food consumption to estimate the intake of PCDD/Fs and dioxin-like compounds.

2.3.1.9.3 Soil concentration

Surface-soil sampling is usually performed by pre-cleaned stainless-steel shovels (Denys et al., 2012; Li et al., 2012). The depth of the samples is conventionally 10 cm, both because of the low mobility of POPs in the soil and because of the importance of surface soil from the point of view of the food chain. Analogously to soil concentrations, the extraction and the analyses of the atmospheric deposition samples is carried out through the US EPA Methods 1613 and 1668B (Zhang et al., 2009; Liu et al., 2012; Rada et al., 2015). In addition to being regulated by the environmental legislation to assess soil quality, the concentration of PCDD/Fs and dioxin-like compounds in soil can be directly used to estimate the accidental soil ingestion by humans and animals and the consequent accumulation in the food chain (Eq. 2.8, Eq. 2.9, Eq. 2.15, Eq. 2.17 and Eq. 2.19).

2.3.1.9.4 Sediment concentration

The standard analytical methods used in the measurement of soil concentration and deposition (US EPA methods 1613 and 1668B) are still commonly adopted also for analyses on sediments (Argiriadis et al., 2014), even though an alternative method for extraction was recently adopted by Friedman and Lohmann (2014). What substantially differs from other media is the sampling method, which is conventionally made by manual core drilling, in accordance with the US EPA standard operating procedure (SOP) 2016 (US EPA, 1994b) or with the more recent SOP SRC-OGDEN-04 (Syracuse Research Corporation, 2001). In addition to being a low-cost methodology, the analysis on sediments can provide indications on the contamination level of aquatic ecosystems and, hence, of fishes. However, further research is needed to estimate the interaction between contaminants in sediments and aquatic organisms.

2.3.1.9.5 Modelling

As an alternative, the exposure assessment can be based on the modelling approach with validation by on-field measurements. The modelling approach requires the identification of the dominant emission sources of the area of study. The first step consists in retrieving information on the type of emission source to be modelled (point, area, line or volume source) and on the way the contaminants of interest are released into the environment (continuous or discontinuous release, presence of chimneys, temperature of the off-gas, outgoing velocity). The second step consists in retrieving emission data or, in the absence of measurements, emission factors representing the emission sources as more accurately as possible. The third step concerns the choice of the dispersion model, which should be suitable for the characteristics of the morphology of the area of study, for the source type of interest, for the desired resolution, for the extension of the domain and for the kind of pollutant (chemically inert or reactive). Examples of dispersion models are AERMOD, CALPUFF, CALGRID, ADMS and AUSTAL2000, even though several other models are available. The fourth step consists in retrieving the meteorological data required by the model pre-processor. Morphological data are also necessary at this stage to calculate wind fields. Additional information, such as the definition of the deposition velocities or the gas/particle partitioning, may usually be defined or modified in the model settings. The model can then be run and the results should be subsequently compared with on-field data; if necessary, the model should be re-run after calibration. If the approach stopped at this stage, no estimations of the level of exposure could be derived; however, it would be possible to obtain indications on the presence/absence of potential critical situations of exposure. Estimations on the oral intake are conventionally pursued by applying food-chain models. The environmental compatibility of human activities can consequently be determined.

2.3.1.9.6 Estimation of the intake by food-chain models

The estimation of the exposure to a certain substance or a group of compounds must consider all the relevant routes of intake. The estimation of the total cancer risk is calculated by summing up the contribution of each route of exposure, taking into consideration that a route of exposure may be contaminated though different pathways.

The inhalation route is only affected by contamination of the ambient air. Therefore, the estimation of the cancer risk through the definition of the URs (Eq. 2.1) or the comparison with the *RfC* for non-cancer risk is immediate. However, the determination of the cancer risk through the definition of SF (Eq. 2.3) or the comparison with the *RfD* for non-cancer risk requires information on the exposure, *e.g.*, indication of the inhalation *IR*, *ED*, *EF*, *BW* of the reference population.

Determining the intake by ingestion, which is the dominant route of exposure to POPs, is more complex: diet is an indirect exposure route that is, on its turn, contaminated through different pathways. Fruit, cereals and vegetables can be contaminated through two main processes: root uptake from soil and atmospheric deposition. Grass is subject to the same pathways of contamination, even though food-chain models attribute the majority of the contamination to atmospheric deposition (Slob and Van Jaarsveld, 1993). Since grass is the primary food for cattle and livestock, the POPs present in grass contaminate the diet of animals; accidental ingestion of soil contributes also to POP intake by animals; consequently, POPs accumulate in their fat tissues and pass to milk or eggs; meat, milk, dairy products and eggs, as well as fruit, cereals and vegetables (in minor contribution) works as carriers of POPs to the human body. Accidental soil ingestion, more probable in children than in adults, represents an additional route of exposure.

The traditional methodologies for the intake estimation through the diet make use of food-chain models developed during the last 25 years. The total concentration of POPs in soil (C_s) can be estimated by the following reservoir model based on long-term deposition data (Lorber et al., 2000):

$$C_s = D_{LT} \frac{1 - \exp\left(-k \cdot t_d\right)}{k \cdot M} \qquad \text{Eq. 2.8}$$

where D_{LT} is the mean total deposition flux (expressed in pg WHO-TEQ m^{-2} y^{-1}), k is the mean annual soil dissipation rate (assumed equal to 0.02772 y^{-1}, corresponding to a PCDD/F half-life time of 25 y), t_d is the time since the deposition D_{LT} has been achieved and M is the soil mixing mass (assumed equal to 112.5 kg m^{-2}) (Lorber et al., 2000). The intake rate of PCDD/Fs and dioxin-like PCBs through soil ingestion by humans ($IR_{h,s}$) can be calculated by the following expression:

$$IR_{h,s} = C_s \cdot I_{h,s} \qquad \text{Eq. 2.9}$$

where $I_{h,s}$ is the average daily soil ingestion rate by humans. $I_{h,s}$ can be assumed as equal to 85 mg d^{-1} for children (Thompson and Burmaster, 1991) and to 50 mg d^{-1} for adults (US EPA, 1997).

The intake of PCDD/Fs and dioxin-like PCBs through consumption of contaminated cereals, vegetables and fruit can be estimated by firstly calculating the concentrations of the pollutants that enter the plant. The concentration of each "*j*" congener due to root uptake ($C_{p,r,j}$) can be estimated by the following expression (UK Environment Agency, 2009):

$$C_{p,r,j} = C_{s,j} \cdot BCF_{p,j} \qquad \text{Eq. 2.10}$$

where $C_{s,j}$ is the soil concentration of the "*j*" congener and $BCF_{p,j}$ is the soil-to-plant concentration factor of the "*j*" congener, depending on the type of vegetable (green vegetable, root vegetable, tuber, tree fruit or herbaceous fruit) and retrievable from Harrad and Smith (1997). As a general definition, *BCF* is the ratio between the concentration of a pollutant in a plant or animal tissue and its concentration in an environmental medium (Davies and Dobbs, 1984).

The concentration deriving from the deposition can be estimated by summing up two contributions: the dry gaseous deposition ($C_{p,dg,j}$), which has to be calculated for each congener, and the particulate deposition ($C_{p,p}$), defined by the following equations:

$$C_{p,dg,j} = \frac{B_{vpa,j} \cdot C_{a,j}}{\rho_a}\left(1 - \frac{c \cdot S_t}{P_{s,j} + c \cdot S_t}\right) \qquad \text{Eq. 2.11}$$

$$C_{p,p} = \frac{D_{LT} \cdot R_p}{Y_p \cdot k_p}\left[1 - \exp\left(-k_p \cdot t_p\right)\right] \qquad \text{Eq. 2.12}$$

where $B_{vpa,j}$ is the congener-specific air-to-leaves transfer factor, $C_{a,j}$ is the congener-specific concentration in ambient air, ρ_a is the air density, c is the Junge's constant ($1.7 \cdot 10^{-4}$ atm cm), S_t is the surface area of the particulates (which can be assumed as $3.5 \cdot 10^{-6}$ cm^2 cm^{-3}), $P_{s,j}$ is the congener-specific saturation vapour pressure of sub-cooled liquid, R_p represents the interception rate of particles by the vegetation (which can be assumed as 0.51), k_p is the loss rate for the plant surface particles (which can be assumed as 126.6 y^{-1}), t_p is the exposure time of the vegetation to deposition per single harvest (0.12 y) and Y_p is the aerial biomass of grass (which can be assumed as 0.25 kg m^{-2}) (Lorber et al., 1994; Harrad and Smith, 1997; Meneses et al., 2002). Congener-specific values of B_{vpa} are provided by Harrad and Smith (1997). The intake rate through consumption of vegetables and cereals by humans ($IR_{h,v}$) can be calculated by summing the product between the average daily consumption ($I_{h,v,k}$) of each of the four "*k*" categories of vegetables (green vegetable, root vegetable, tuber and herbaceous fruit), the sum of the total concentrations $C_{p,r}$, $C_{p,dg}$, $C_{p,p}$ in each of the four categories, estimated by Eq. 2.10, Eq. 2.11 and Eq. 2.12, and a coefficient representing the fraction of vegetable product coming from the contaminated area with respect to the total vegetable products consumed ($L_{h,v,k}$):

$$IR_{h,v} = \sum_{k=1}^{4}\left[L_{h,v,k} \cdot I_{h,v,k}\left(C_{p,r,k} + C_{p,dg,k} + C_{p,p,k}\right)\right] \qquad \text{Eq. 2.13}$$

With regards to fruit, the intake rate ($IR_{h,f}$) can be calculated by the fraction of fruit coming from the contaminated area with respect to the total fruit consumed ($L_{h,f}$), the average daily fruit consumption ($I_{h,f}$) and the sum of the total concentrations due to the contribution of root uptake ($C_{p,r,f}$) and of the uptake from air and the stem ($C_{p,as,f}$):

$$IR_{h,f} = L_{h,f} I_{h,f}\left(C_{p,r,f} + C_{p,as,f}\right) \qquad \text{Eq. 2.14}$$

$C_{p,as,f}$ can be calculated through a more complex model, whose detailed methodology is reported by Trapp (2007).

The intake of POPs through consumption of milk and dairy products can be estimated by calculating the concentration of POPs in milk fat and then considering the fraction of fat in each kind of product. The total concentration in milk fat (C_{mf}) can be estimated by the following expression (Slob and Van Jaarsveld, 1993):

$$C_{mf} = \frac{b_{mf}\left(A_g \cdot c_g \cdot D + I_{c,s} \cdot C_s\right)}{f_{f,m} \cdot P_m} \qquad \text{Eq. 2.15}$$

where A_g is the average area grazed by one cow per day (which can be assumed as 100 m^2 d^{-1}, approximately), c_g is the fraction of A_g covered with grass (assumed as 0.9), D is the mean daily deposition, $I_{c,s}$ is the average soil ingestion by the cow (about 225 g d^{-1}), $f_{f,m}$ is the fraction of fat in cow's milk, P_m is the average daily milk production (about 20 kg d^{-1}) and b_{mf} is the bioavailability of POPs in milk fat, which is the fraction of contaminant present in milk fat with respect to the amount ingested by the animal (Hoogenboom et al., 2006; Slob and Van Jaarsveld, 1993). Differently from the *BCF* concept, b_{mf} considers the absorption by the digestive tract and the metabolism (McLachlan, 1997). Average values of b_{mf} are listed in Kerst et al. (2004). A mean value of 0.35 was established by the German guideline VDI 2310-46 for 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF, the most toxic congeners (VDI, 2005). The calculation of C_{mf} can be refined by summing up the congener-specific contributions after applying congener-specific b_{mf} values, like those provided by McLachlan (1997) as a result of previous studies. The POP intake rate though consumption of milk and dairy products by humans ($IR_{h,md}$) can finally be estimated:

$$IR_{h,md} = C_{mf}\left(L_{h,m} \cdot I_{h,m} \cdot f_{f,m} + \sum_{l} L_{h,d,l} \cdot I_{h,d,l} \cdot f_{f,d,l}\right) \qquad \text{Eq. 2.16}$$

where $L_{h,m}$ is the fraction of milk produced in the contaminated area over the total milk consumed, $I_{h,m}$ is the average daily milk consumption by humans, $L_{h,d,l}$ is the fraction of the "*l*" type of dairy product coming from the contaminated area over the total amount of the "*l*" dairy product consumed, $I_{h,d,l}$ is the average daily consumption of the "*l*" type of dairy product and $f_{f,d,l}$ is its respective content of milk fat.

A food-chain model to determine the concentration in meat was proposed by McLachlan (1997). The model calculates the total concentration of POPs in beef fat (C_{bf}) through an integral over the time (t) till the lifetime of the animal (T):

$$C_{bf} = \frac{b_{bf}}{f_{f,b}} \int_{t=0}^{T} \left(A_g \cdot c_g \cdot D + I_{c,s} \cdot C_s\right) dt \qquad \text{Eq. 2.17}$$

where $f_{f,b}$ is the mass fraction of fat in beef and b_{bf} is the bioavailability in beef fat (McLachlan, 1997). Congener-specific values of b_{bf} were proposed by Slob et al. (1995). The intake rate of POPs by beef consumption ($IR_{h,b}$) results in:

$$IR_{h,b} = L_{h,b} \cdot C_{bf} \cdot f_{f,b} \cdot I_{h,b} \qquad \text{Eq. 2.18}$$

where $L_{h,b}$ is the fraction of beef coming from animals grown in the contaminated area over the total amount of beef consumed, $f_{f,b}$ is the content of fat in beef and $I_{h,b}$ is the average daily consumption of beef.

The total concentration of POPs in eggs (C_e) was modelled by Harrad and Smith (1997) and is described by the following expression:

$$C_e = BCF_e \cdot f_{y,e} \left[\left(F_s C_s + F_g C_g + F_f C_{fg} \right) \right] \qquad \text{Eq. 2.19}$$

where BCF_e is the concentration factor of the egg yolk, $f_{y,e}$ is the average mass fraction of yolk in the egg (assumed as equal to 0.3) , C_g is the total POP concentration in grass, C_{fg} is the total POP concentration in fodder or grain (which can be estimated as the sum of $C_{p,r}$, $C_{p,dg}$, $C_{p,p}$) and F_s, F_g and $F_{f\,g}$ are the fractions of the chicken's diet that is soil ingestion, grass and fodder or grain, respectively. Values of F_s, F_g, F_{fg} and congener-specific values of BCF_e are reported by Harrad and Smith (1997). The intake rate of POPs by egg consumption ($IR_{h,e}$) results in:

$$IR_{h,e} = L_{h,e} \cdot C_e \cdot I_{h,e} \qquad \text{Eq. 2.20}$$

where $L_{h,e}$ is the fraction of eggs coming from animals grown in the contaminated area over the total amount of eggs consumed and $I_{h,e}$ is the average daily consumption of eggs by humans.

Due to the complexity of species and of the aquatic ecosystem, no model is currently available to estimate the intake by fish consumption, even though important contributions to the daily intake of PCDD/Fs and dioxin-like PCBs were demonstrated to derive from this route in several case studies (Godliauskiene et al., 2012; Marin et al., 2011; Sasamoto et al., 2006).

2.3.1.10 Critical aspects of the conventional monitoring approach and of the current environmental legislation

As previously stated, a systematic monitoring activity on the POP content of food would require time and high costs for routinely inspections and analyses. Hence, alternative solutions must be developed and, possibly, taken as a reference for regulatory purposes. Ambient air concentrations and deposition fluxes could be an important source of information on the pollution level of the environment and, indirectly, of the food chain. Unfortunately, until now, at the European level no regulation officially has been set on PCDD/Fs air concentrations and deposition fluxes. Therefore, the preservation of the food chain currently relies only on local regulations regarding soil concentration and on random inspections on the PCDD/F concentration in food (Section 2.3.1.6).

Emission limits for the critical emission sources that have been recently highlighted (*e.g.*, MBT plants, wood burning) should be adopted, for instance by extending the emission limit values already established by some countries, at least with regards to MBTs (*e.g.*, Germany and Austria).

A correspondence between the IARC classification of the PCDD/F and dioxin-like PCB congeners and the respective TEFs should be checked, since there is the risk that the effect of some congeners might be underestimated; in addition, the last revision of the TEFs dates back to 2005, whilst the IARC classification has been recently updated.

Some critical considerations could also be expressed on the most known decisional tool: Life Cycle Assessment (LCA). As recently pointed out (Schiavon et al., 2014b), although LCA is a powerful tool to evaluate and compare the environmental impacts of different processes, the choice of the best option should not be limited to its results: for instance, the results of dispersion modelling studies, carried to simulate the dispersion of PCDD/Fs from MBT plants, showed potentially high impacts on the areas surrounding such facilities (Rada et al., 2011; Ragazzi et al., 2014b). The local impacts of MBTs may be comparable with the impacts expected from the latest MSW incinerators, due to the different APC technologies in use, the way the effluents are released into the atmosphere, the relative proximity of dwellings, fields and pastures (usually more common around MBT plants) and the absence of specific regulations. Emission, dispersion and exposure models could help interpreting and integrating the indications of an LCA.

Finally, there is great uncertainty on the estimation of the locally-produced food that is consumed by a target population; this last aspect has repercussions on the estimation of the daily intake and, therefore, on the overall exposure assessment; a synergistic approach between capillary networks of deposimeters and food traceability should be implemented to overcome this issue.

2.3.1.11 Novel options for exposure assessment

During the last decades, advances have been made in the development of tools for the exposure assessment. It being understood that the classical monitoring approaches described at the beginning of Section 2.3.1.9 still represent an undeniable fundamental point in the exposure assessment, new approaches, integrative tools or simplifying methodologies can help detecting the presence of critical situations of exposure, identifying the dominant emission sources, proposing design criteria for critical activities and defining limit values to assure an acceptable risk level.

In particular, novel monitoring approaches have been proposed during the last decade. Researchers have investigated the potential of conifer needles as passive-sampling alternative to determine the spatial and temporal variability of mean concentrations of PCDD/Fs and PCBs by means of internal analytical procedures (Rappolder et al., 2007; Klánová et al., 2009; Bertolotti et al., 2014). The results of a monitoring campaign carried out in Germany on conifer needles of different ages were comparable with the time series recorded by the German Dioxin Database (Rappolder et al., 2007); as an added value, a wider area could be covered by this monitoring method. In another study, conifer needles were compared to passive samplers with polyurethane foam, which revealed to be less efficient than conifer needles in collecting particle-bound POPs (Klánová et al., 2009).

An additional and alternative method is represented by the biomonitoring performed with lichens exposed to contaminated air. Indeed, lichens are able to accumulate radionuclides, metals and POPs (Conti and Cecchetti, 2001). This method showed interesting results in three recent studies (Augusto et al., 2007, 2009; Denys et al., 2012). A practical application of this methodology, concerning the area of Setúbal (Portugal), provided a risk map that would have required the adoption of several deposition samplers to cover the region investigated (Augusto et al., 2007). Another kind of biomonitor, consisting in an endemic Bromeliad species, was placed in funnels to measure atmospheric deposition of POPs: the deposition measured with this methodology was comparable with the results of conventional deposition measurements (de Souza Pereira et al., 2007a, 2007b), although applications of this method are limited to one case study.

A proposal for the development of a novel kind of deposimeter was made in a recent study by Rada et al. (2014a), who proposed the integration of a remotely controlled coverage and a webcam for video surveillance to quantify the contribution of a dominant and intermittent punctual source (*e.g.*, industrial plant, energy production plant, incinerator) with respect to periods of inactivity of the plant. Vassura et al. (2011) and Rada et al. (2014a)[2] also presented the potentialities of crossing the congener profiles measured in PCDD/F and PCB depositions with the typical fingerprints or measured congener profiles in the emissions of a specific activity present in the surroundings of the monitored area, in order to facilitate the estimation of the dominant source. In a similar experience, congener profiles and diagnostic ratios of POPs measured in the sediments of a pond, were recently studied and successfully applied to investigate the dominant sources in an Alpine valley (Argiriadis et al., 2014). Analyses on sediments at different depths showed to be useful to understand the evolution of PCDD/F emissions in an area over the years: the results obtained by Argiriadis et al. (2014)[3] were in agreement with the evolution of the emissive framework of the area investigated, where POP emissions decreased starting from 2009, when an important steel plant in that area adopted the BATs.

Alternative analytical strategies, based on the concept of biomonitoring, have been developed and tested. The most important one is the CALUX (Chemically Activated LUciferase gene eXpression) bioassay, based on a genetically modified cell line inducing luciferase when responding to dioxin-like compounds (Han et al., 2004); a new CALUX bioassay was recently used in place of the conventional GC-HRMS analyses (Croes et al., 2012). The classical approach considers the US EPA methods 1613 and 1668B (US EPA, 1994a, 2008) as the conventional analytical methodologies to determine PCDD/Fs and PCBs, respectively. The CALUX bioassay makes use of an alternative methodology based on a C18 filter, to minimize the use of organic solvent and lower the toxicity towards the cells (Croes et al., 2011).

The opportunities offered by analyses on PCDD/F and PCB concentrations in the sewage sludge of wastewater treatment plants were recently investigated: in particular, it was demonstrated that the comparison of sewage-sludge samples from uncontaminated and potentially contaminated regions is able to quickly highlight the presence of critical levels of exposure, since the POPs present in the wastewater (and thus in the diet of a population) are finally concentrated in the sewage sludge (Rada et al., 2013a). This methodology was applied to a study area where a steel plant is present: in this specific case, a sensitivity analysis of this method showed that, if the population was exposed to a concentration of POPs in food that is 100-time higher than an unexposed population, a 15-time higher concentration would be observed in the sewage sludge of the wastewater treatment plant serving the population exposed (Rada et al., 2013a)[4].

Useful insights into the choice of the location of an activity or of the adequate APC technologies to be adopted by a stationary emission source can be obtained by coupling dispersion modelling with risk indicators: in three recent studies (Rada et al., 2011; Ragazzi et al., 2014a; Schiavon et al., 2015b)[5], the low capability of open biofilters (traditionally adopted in MBTs) in diluting the effluent released into the atmosphere

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[2] This methodology will be explained in details at Section 3.3.

[3] This methodology will be explained in details at Section 3.4.

[4] This methodology will be explained in details at Section 3.2.

[5] The results of the works carried out by Ragazzi et al. (2014a) and Schiavon et al. (2015b) will be presented at Sections 5.2 and 5.3, respectively.

was highlighted, as well as the consequent potential impacts on the surrounding region in terms of PCDD/F deposition.

Coupling edited food-chain models with data on the food consumption resulted in a recent proposal for a PCDD/F deposition limit value, specifically based on the typical diet of a target population (Schiavon et al., 2013)[6]: consolidated food-chain models (Slob and Van Jaarsveld, 1993; Lorber et al., 1994, 2000; Harrad and Smith, 1997; Trapp, 2007) were edited to be run backwards by starting from the food consumption of a population and from the TDI proposed by the WHO, determining the acceptable PCDD/F concentration in the food consumed, till deriving a region-specific acceptable value for PCDD/F deposition (Schiavon et al., 2013). This approach differs from that adopted in Belgium by De Fré et al. (2000) and Van Lieshout et al. (2001), since the acceptable deposition value is calculated by starting directly from the TDI and not by starting from a deposition value and obtaining the corresponding TDI by iterations.

Table 2.3 summarizes the benefits and the potential limitations of the novel methodologies here presented compared with the conventional monitoring approaches. While conventional methodologies generally provide only current and punctual information on the contamination levels of an area, the integration of the traditional approach with these novel methodologies allows extending the significance of the data collected by conventional monitoring methodologies over time and space. This is the case, for instance, of the analysis on sediment layers, of the adoption of dispersion models and of strategies based on the use of a widespread network of low-cost and natural sampling systems, such as conifer needles and lichens. Methods such as the CALUX bioassay and analysis on sewage sludge samples are low-cost analytical and monitoring options for a preliminary assessment, before adopting conventional and more accurate monitoring methods, if necessary. Methodologies like the use of food-chain models, the determination of diagnostic ratios and congener profiles even allow retrieving information that conventional methodologies alone do not.

2.3.2 Benzene

2.3.2.1 Introduction

Between 1982 and 1987, the IARC classified benzene as belonging to Group 1, since evidences demonstrated that such compound is carcinogenic to humans (IARC, 2015a).

Road traffic, wood burning, industrial activities and smoke of cigarette are some of the most important benzene emission sources and exposure contributors to this pollutant. Benzene has been widely employed as an industrial solvent in paint, lacquer thinners, varnishes and gasoline and it is currently used as a raw material in the synthesis of alkyl benzenes, aniline, cyclohexane, phenol, styrene and to produce detergents, plastics and resins (Sarigiannis et al., 2011). The exposure of people living and/or working in environments characterized by the presence of such sources represents a risk factor for the development of leukemic forms. Although the levels of benzene in ambient air have been decreasing from the last decade (mainly because of

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[6] This methodology will be explained in details at Chapter 4.

Table 2.3: Benefits and possible limitations of the novel methodologies for exposure assessment here presented in comparison with the conventional monitoring approach.

Novel methodologies		**Comparison with conventional methodologies**	
Environmental matrix / Tools	**References**	**Benefits**	**Limitations**
Conifer needles	Rappolder et al. (2007); Klánová et al. (2009); Bertolotti et al. (2014)	Low-cost methodology improving the spatial resolution of the sampling; capability of estimating the temporal evolution of pollutant levels in the past	Possible underestimation of concentrations due to rain and wind removal
Lichens	Conti and Cecchetti (2001)	Low-cost methodology improving the spatial resolution of the sampling	Calibration through conventional methodologies is required
Diagnostic ratios and congener profiles	Argiriadis et al. (2014); Rada et al. (2014a)	Quick estimation of the dominant source in the sampling area, not possible with the conventional monitoring approach alone; capability of estimating the temporal evolution of pollutant levels in the past (sediments only)	The estimation of past contamination levels requires the dating of sediment layers
CALUX bioassay	Croes et al. (2011, 2012)	Quick, sensitive and low-cost analytical methodology that can be used as a convenient alternative to GC-HRMS	Calibration through conventional methodologies is required
Sewage sludge	Rada et al. (2013a)	Low-cost methodology to detect anomalous levels of exposure via diet	Possible interferences from external factors (*e.g.*, non-residential population); acute episodes of exposure cannot be observed
Dispersion models and risk indicators	Rada et al. (2011); Ragazzi et al. (2014a)	Easy and spatially-resolved assessment of local criticalities in terms of air quality and deposition; possibility of simulating scenarios and predict future trends	Calibration through conventional methodologies, emission factors, morphology and meteorological data are required
Atmospheric deposition and food-chain models	Schiavon et al. (2013)	Capability of determining a safe deposition value to preserve the agricultural and livestock food chains from contamination	Information on the origin of food and statistics on the local diet are required

the benzene content reduction in gasoline), potential critical situations still can exist locally and can elude the control activity carried out by the traditional monitoring networks.

2.3.2.2 Health effects

The main pathway of exposure to benzene is inhalation. The most severe health effects of benzene are related to chronic exposure. Acute toxicity is of minor importance, because serious adverse effects require exposure at very high concentrations, which difficultly are found in the environment and in workplaces: in fact, fatal acute exposure can occur only at concentrations higher than 60,000 mg m^{-3} (Chilcott, 2007). The main risk, in terms of mortality, is due to a chronic exposure at lower concentrations.

Benzene is a genotoxic carcinogen. Its genotoxicity has been extensively studied and some results demonstrate chromosomal effects at mean occupational exposures of 4-7 mg m^{-3} (European Environment Agency, 2007). Recent in-vivo data indicate also that benzene is mutagenic. But its more reported effects are hematotoxicity and leukaemia: changes in blood and bone marrow consistent with hematotoxicity have been recognized in humans and experimental animals. Clinical outcomes observed are leukopenia, thrombocytopenia, anaemia, and aplastic anaemia (Agency for Toxic Substances and Disease Registry, 2007). In addition, a substantial number of case reports and epidemiological studies provide evidence of a causal relationship between occupational exposure and various types of leukaemia (Chilcott, 2007).

The first epidemiological study evaluating benzene effects started in 1977 and involved a cohort of workers of a manufacture in Ohio, exposed from the 1950s to benzene during the production of Pliofilm, a natural rubber film (Infante and White, 1983). The incidence of leukaemia cases was significantly in excess of the expected number of cases based on U.S. general population death rates (Infante and White, 1983). Occupational exposure to significantly elevated levels of benzene shows association with acute myeloid leukaemia, which is the most frequently reported form of leukaemia related to benzene exposure (Johnson et al., 2009). But also cases of chronic myeloid leukaemia, chronic lymphocytic leukaemia, multiple myeloma and non-Hodgkin lymphoma have been found in people chronically exposed to benzene (Baan et al., 2009). Another important epidemiological survey is the Health Watch prospective cohort study, that was carried out in Australia (Glass et al., 2005). The study started in 1981 and refers to 18,000 employees who have worked for more than five years in the petroleum industry; the survey was repeated in 1986, 1991 and 1996 and the collected data provide evidence of an association between occupational exposures to average concentrations > 51 mg m^{-3} and increased risk of leukaemia (Glass et al., 2005).

The mechanism of the leukaemogenic effects of benzene is not totally understood. Biotransformation in liver is thought to be a necessary step to the hematotoxicity and carcinogenicity of this compound (Caprino and Togna, 1998). The inhalation of benzene may stimulate cytochrome P450 2E1, which oxidizes benzene and generates oxygen radicals. Cytochrome P450 2E1, together with quinone oxidoreductase, are particularly implicated in the mechanism of benzene toxicity: the absence of the first one entails a reduction of the cytotoxic and genotoxic effects in mices; on the other hand, susceptibility to benzene toxicity is increased in humans and animals lacking quinone oxidoreductase (Chilcott, 2007). Even though the metabolite responsible for the carcinogenicity of benzene has not been definitively identified, some evidences show that its effects are mediated by benzene epoxide, a reactive metabolite of cytochrome P450 2E1 (Chilcott, 2007). The reactive oxygen species that are formed during the metabolism of benzene seem to have direct influence in the DNA damage: indeed, these species may bind covalently to macromolecules, including proteins and DNA. The direct attack on DNA may give rise to oxidative damage or to double-strand breaks (Andreoli et al., 1997; Ross, 2000; Angelini et al., 2012). DNA damage is the key mechanism of benzene genotoxicity which leads to hematotoxicity and leukaemia. Genetic variations in DNA-repair genes have also indirect influence on benzene-induced DNA damage. In light of this, some studies evaluated the effect of polymorphisms in

DNA-repair genes on the formation of micronuclei, which may be adopted as biomarkers of early biological effects of the exposure to benzene (Angelini et al., 2012; Violante et al., 2003).

2.3.2.3 Atmospheric fate

Vaporized atmospheric benzene may persist for minutes in street canyons, for hours in an urban area and up to one week outside. This allows benzene to be transported over long distances and elevated concentrations in remote sites could be observed as a consequence (European Environment Agency, 2007). The lifetime of benzene is dependent upon the concentration of atmospheric ·OH radicals, which are the primary reactants for airborne benzene (Johnson et al., 2009). The natural atmospheric removal process starts, in presence of solar radiation, with the addition of an ·OH radical to the aromatic ring and with the subsequent reaction with NO_2; in this way, phenol and nitrobenzene are formed; then, ring cleavage leads to the formation of glyoxal, formaldehyde and maleic anhydride (Agency for Toxic Substances and Disease Registry, 2007). A second route may start from the reaction with NO_3, which takes to the formation of nitrobenzene, nitro and di-nitro phenols (Agency for Toxic Substances and Disease Registry, 2007). The reaction with ·OH radicals occurs during daylight hours, whilst benzene reacts mainly with NO_3 during evening and night-time hours (Atkinson and Arey, 2007).

2.3.2.4 Limit values in the environment

The European legislation established an annual mean concentration limit value for benzene in ambient air as equal to 5 µg m^{-3} (European Union, 2008). In the last years, due to concern for its genotoxic and carcinogenic behaviour, efforts have been made in order to reduce the occupational exposure of workers to benzene. The American Conference of Governmental Industrial Hygienists established two kinds of Threshold Limit Values (TLVs) for the occupational exposure to benzene: the Time Weighted Average TLV (TLV-TWA) represents the limit value based on the mean concentration weighted on time referred to a workday or a workweek; the Short Time Exposure Level TLV (TLV-STEL) represents the limit value based on a TWA concentration of 15 minutes. The limit values for TLV-TWA and TLV-STEL are respectively 0.5 ppm and 2.5 ppm, equivalent to 1.6 mg m^{-3} and 8 mg m^{-3} at standard temperature and pressure conditions (Occupational Safety & Health Administration, 2012). At a European level, the Directive 97/42/EC established a limit value for occupational exposure of 1 ppm (3.25 mg m^{-3}) averaged on an 8-hour period (European Union, 1997).

2.3.2.5 Traditional and emerging emission sources

It is estimated that anthropogenic sources account for over 90% of airborne benzene and incomplete burning from combustion is the most significant source (European Environment Agency, 2007). In fact, benzene is present in gasoline as antiknock. In Europe and in the U.S.A., the benzene content is limited to percentages lower than 1%. Road traffic is the most important contributor in urban areas. PAHs are formed during the combustion processes, while monocyclic aromatic hydrocarbons and alkylated-PAHs may be largely released from unburned fuel (Atkinson and Arey, 2007). At European and North-American level, traffic-related benzene accounts for more than 80% of the total emissions (Agency for Toxic Substances and

Disease Registry, 2007; European Environment Agency, 2007). Due to its proven carcinogenicity, this pollutant is considered the most hazardous component of the traffic-related air pollutants (Angelini et al., 2012). Additional point sources usually present in urban areas are industrial sources (especially petrochemical plants) and evaporation of benzene from crude oil leaks and automobile refuelling stations, which may be considered an important source of personal exposures, together with cigarette smoke: in fact, although it contributes to only 0.1% of benzene emissions, cigarette smoke is estimated to account for the 40% of personal exposure (Agency for Toxic Substances and Disease Registry, 2007; Johnson et al., 2009). Regarding the waste sector, industrial waste landfills and waste incinerators represents the most important sources of benzene, even though some studies also pointed out the role of other waste treatments, such as biodrying and biostabilisation (He et al., 2010; Pierucci et al., 2005; Ragazzi et al., 2011). Domestic burning for heating purposes is responsible for 3-7% of benzene emissions in Europe, although this is an estimation of the average contribution: in Scandinavian countries, for example, wood burning for heating purposes reaches over the 50% of the total benzene emissions (European Environment Agency, 2007); the same phenomenon may occur also in rural and mountainous settlements in the rest of Europe.

2.3.2.6 Typical levels in the environment

High levels of benzene are commonly found in developing countries, due to obsolete car fleets and the large number of vehicles present in urban areas. Mean concentrations measured in Delhi during February 2005 were comprised between 3 and 35 µg m^{-3}, with a mean of 21.4 µg m^{-3} during the whole year (Indian Ministry of Environment & Forests, 2008). The mean concentration in residential locations resulted in 12.4 µg m^{-3}, while in roadside areas the concentration increases to 34.6 µg m^{-3}. Higher concentrations were measured in residential/commercial areas in Bangalore (70 µg m^{-3} on average) (Indian Ministry of Environment & Forests, 2008). Rush hour concentration up to 42.4 µg m^{-3} were measured in Bangkok, where traffic is dominated by two-strokes motorcycles, whilst non-rush hour concentrations were comprised between 16.3 and 30.9 µg m^{-3} (Leong et al., 2002). However, very high peak concentrations may be reached also in European urban areas, especially within urban street canyons and nearby tunnel portals: elevated benzene concentrations (up to about 100 µg m^{-3}) were measured during rush hours in a trafficked street canyon of Ioannina (Greece) (Kassomenos et al., 2004); high average concentrations (greater than 10 µg m^{-3}) were measured in a street canyon of Paris during October 2001 (Vardoulakis et al., 2005); average concentrations measured nearby two tunnel portals in Naples showed a maximum of 23.5 µg m^{-3} and a mean value of 14.2 µg m^{-3} and these results presented a correlation with the two-wheeler vehicle flow (Murena, 2007).

To investigate the influence of traffic (the prevailing outdoor source in urban areas) on indoor concentrations, several studies were carried out on non-smoker participants: in Amsterdam (the Netherlands), mean concentrations of 5.7 and 3.0 µg m^{-3} were measured outside high traffic and low traffic exposed houses respectively, while the corresponding indoor concentrations were 7.7 and 5.7 µg m^{-3} (Fischer et al., 2000); a study on citizens of several European cities showed that the average indoor benzene concentration can be 1.51 times higher than outdoor (Cocheo et al., 2000); one study on four French cities also highlights the difference between personal exposure and outdoor mean concentration, the first being 2.7-3.5 times higher than the second one (Gonzalez-Flesca et al., 2007); a study carried out in Florence (Italy) showed that indoor pollution and transportation means contribute significantly to individual exposure levels, especially in winter season (Fondelli et al., 2008); on the other hand, home concentrations were found to be lower (6.0-13.1 µg m^{-3}) than outdoor levels (20.4 µg m^{-3}) in Athens (Greece) (Chatzis et al., 2005); a study on six European cities showed also the important role of commuting in the personal exposure to benzene, that may be 1.5 times higher than the exposure occurring in background environments (Pérez Ballesta et al., 2006). The measured outdoor levels encountered in these studies are close to or exceed the limit value of 5 µg m^{-3}. The higher levels encountered in indoor environment could be explained by considering both the presence of other indoor sources (*e.g.*, domestic heating, cooking activities or use of solvents) and the use of adsorbent materials for wall and floor covering (*e.g.*, wallpaper, carpets or moquette), which is especially common in central and northern Europe and uncommon in Mediterranean countries (Chatzis et al., 2005). This may explain the difference in the results obtained in Athens.

Petrol filling stations represent important point sources of benzene. In urban areas, especially, their emissive contribution adds up to that of road traffic. In this context, benzene may evaporate from the fuel tanks of cars and petrol stations. Although petrol stations are known as one of the most significant sources of hydrocarbons (and consequently benzene) in an urban environment, only a few studies outline their contribution to benzene concentrations in their vicinity. Srivastava et al. (2006) found a very high mean concentration (up to 540 µg m^{-3}) at petrol pumps in Mumbai (India). It is worth noting that the level of exposure is largely dependent on the technical specifications of gasoline, especially its benzene content, and to the emission control technology, such as vapor recovery systems (Majumdar et al., 2008). In an urban petrol station of Ioannina, the measured mean benzene concentration was 50 µg m^{-3} and the station showed its influence on a radius of tens of meters (Karakitsios et al., 2007a).

Another source of exposure to benzene is wood burning, used for cooking and heating purposes. It has been estimated that approximately 10% of the space heating in urban areas of the northern United States is from wood burning, with up to 50% in smaller, rural towns (Agency for Toxic Substances and Disease Registry, 2007). Benzene has been found to be a major component of the emissions from wood burning and constituted roughly 10-20% by weight of total non-methane hydrocarbons (Barrefors and Petersson, 1995). According to a research carried out during the last decade (Gustafson et al., 2007), almost three billion people rely on solid fuel as their primary source of domestic energy. Wood stoves have also become popular household additions and their use has been encouraged because wood is a renewable resource and its cost is lower than other fossil fuels, especially in regions where wood is abundant. Emissions from charcoal combustion are also of great interest, since benzene is the predominant aromatic compound emitted. For example, according to a study by Olsson and Petersson (2003), concentrations measured above charcoal used for grilling exceeded 10 mg m^{-3}. A monitoring campaign was carried out in a small Swedish village to investigate the contribution of wood burning to the indoor and outdoor concentrations of benzene: significantly higher indoor levels were found in houses that used wood as fuel for domestic heating (mean concentration of 5.7 µg m^{-3}) compared with the reference dwellings (2.5 µg m^{-3}), while mean outdoor concentrations were

1.3 and 1.0 μg m^{-3}, respectively (Gustafson et al., 2007). In a Finnish village, benzene concentrations showed a similar diurnal pattern as the use of wood and the elevated benzene/toluene ratio indicated that wood combustion was the most important source (Hellén et al., 2008): in fact, the benzene/toluene ratio was observed to be 2.2 near wood combustion activities and about 0.3 along trafficked roads, while in this study a ratio of 1.0 was found, indicating that wood burning may contribute for 70% to local benzene sources; furthermore, the benzene pattern did not follow that of MTBE, which has only traffic-related sources (Hellén et al., 2008). Benzene concentrations were also measured during a two-week campaign by passive samplers and the resulting mean concentration was 1.25 μg m^{-3}, with a background level of 1.04 μg m^{-3} (Hellén et al., 2008).

During combustion, any hydrocarbons in the hottest regions of flue gases can rearrange to give initially benzene and then phenols under oxidizing circumstances (Williams et al., 2012). Benzene emissions from wood stoves depend on the technology in use and on the type of fuel. Several studies focused on the measurement of emission factors from stoves: benzene emission factors from various wood burning appliances were reported by Tissari et al. (2007), ranging between 300 mg kg^{-1} (for baking ovens) and 2,500 mg kg^{-1} (for a sauna stove); emission factors from domestic wood burners, between 433 and 1,094 mg kg^{-1}, are reported in by Scott (2005); emission factors from commercial residential boilers were measured, ranging between 0.11 and 91 mg MJ^{-1} when passing from pellet burners to old-type wood boilers (Johansson et al., 2004). Wood pellets burn more efficiently with respect to other wood fuels, such as wood logs. During the flaming phase, wood pellets burn even more efficiently and with lower emissions (Olsson, 2006). Maximal benzene concentrations in smoke from pellets are achieved during after-flame smouldering (above 30 mg m^{-3}) and minimal in the early-flaming phase (below 0.4 mg m^{-3}) (Olsson, 2006). In the light of this, one possible way to decrease the total emissions from combustion of wood pellets is to keep combustion at the flaming combustion stages and to prefer the use of softwood pellets as a fuel.

While municipal waste can be almost completely destroyed by combustion in waste incinerators, trace quantities of incompletely burned products such as aromatic compounds may still be present in the flue gas (Schöbel-Ostertag et al., 2005). In fact, although typical waste incinerators are operated between 1100 and 1250 K at atmospheric pressure with excess oxygen to ensure complete destruction of aromatic compounds, the existence of local cold or fuel-rich regions cannot be ruled out. The conditions occurring in these regions lead to the formation of the first aromatic ring structure, *i.e.*, benzene (Schöbel-Ostertag et al., 2005). Ambient air concentrations were measured nearby the municipal waste incinerator of Tarragona (Spain), resulting in mean values between 0.1 and 3.2 μg m^{-3} (Vilavert et al., 2009). In spite of the potential role of MBTs in the air quality of their surrounding areas, no monitoring activities in the vicinity of MBT plants have been carried out yet. The release of benzene from MBTs was documented by researches carried out during the last decade: a biostabilisation plant located in northern Italy released benzene in concentration of 275 μg Nm^{-3} before passing through a bio-filter and 42 μg Nm^{-3} after the bio-filter (Pierucci et al., 2005). In a biodrying plant, benzene concentrations reached 116 μg Nm^{-3} during the first day of the process, with a second lower peak after 10 days: the first peak could be attributed to the release of inherited aromatics contained in MSW, whilst the second peak is probably due to the evaporation of the dissolved aromatics in water or lipids (He et al., 2010). The low release height of biofilters, combined with the inadequate dispersion of the plume in the atmosphere, may lead to critical concentration levels in the vicinity of MBT plants, as it will be presented at Sections 5.2 and 5.3.

2.3.2.7 Environmental monitoring

The standard methodology used by the conventional air quality monitoring stations for measuring ambient air concentrations of benzene is based on hourly automatic sampling of air and further gas-chromatographic analysis.

Passive sampling techniques represent a valuable alternative, especially if long-term average concentrations are the target of the monitoring activity. In this case, the detail on peak concentrations would be lost, but average concentrations (usually on a timespan of 2-4 weeks) would be conveniently measured. Furthermore, the loss of detail on peak concentrations would be compensated by a gain of detail in the spatial resolution of the samplings, since passive samplers can be installed in several locations at the same time, contrarily to conventional air quality stations.

A more sophisticated method consists in the use of thick-film (or resistive) sensors. The operation principle of thick-film sensors is based on the electrochemical interactions between a semiconductor oxide, atmospheric oxygen (O_2) and the gaseous compound to be analysed. The first reaction occurs at the surface of a semiconductor oxide and involves the transfer of charge from the semiconductor to O_2; consequently, the gaseous compound to be measured binds to O_2 and allows the electrons to be released on the conduction band of the semiconductor oxide (Unitec, 2013). Depending on the gaseous pollutant to be measured, different semiconductors are adopted to ensure proper selectivity to the target compound. In addition, specific catalysts can be used to improve the selectivity (Martinelli and Carotta, 1995; Yang, 2011). Satisfactory results in terms of sensitivity and selectivity to benzene were achieved when adopting a tungsten-based semiconductor coupled with a platinum-alumina catalytic filter (Pt-Al_2O_3) (Ivanov, 2004).

In addition, biomonitoring techniques have been recently tested: blood benzene, urinary trans,trans-muconic acid and urinary S-phenilmercapturic acid (two metabolites of the biotransformation of benzene) have been found as effective biological markers (Ciarrocca et al., 2012).

The cancer risk associated with long-term exposure to benzene can be calculated by the methodology presented in Section 2.3.1.4 and by considering that inhalation represents the main pathway of exposure to this atmospheric pollutant.

2.3.2.8 Critical aspects of the conventional monitoring approach and of the current environmental legislation

The control of air quality has been traditionally committed to networks of fixed air quality stations managed by the public environmental authorities. Since air quality stations are the official monitoring approach recognized by the European legislation to evaluate the compliance with the regulatory concentration limits of air pollutants, the sampling and analytical devices must ensure high-quality standards. Therefore, high-accuracy instruments are adopted, whose quality and proper operation are routinely checked with periodical calibrations. On the other hand, elevate quality standards imply high investment costs of the equipment (Marć et al., 2015). In addition, fixed air quality stations cannot provide adequate spatial detail on the air quality of an area, since their results are only representative of the local situation in the correspondence of the punctual sampling. Some local situations of critical levels of air pollutants may elude the conventional monitoring system with potentially severe consequences on the settled population, which can be exposed to unacceptable concentrations (Ragazzi et al., 2013b). At a European level, the location of the air quality stations is regulated by the environmental legislation. According to the Directive 2008/50/EC of the European Parliament and the Council (European Union, 2008), the lowest number of air quality stations to be placed in a specific area is regulated on the basis of the exceedance of threshold concentration values for each pollutant of interest, among coarse PM (PM_{10}), fine PM ($PM_{2.5}$), O_3, nitrogen oxides (NO_x), CO, sulphur oxides, benzene, benzo[*a*]pyrene, lead and heavy metals, independently of the proximity between emission sources and potential receptors.

2.3.2.9 Novel options for exposure assessment

The sector of the air quality monitoring has recently moved towards the test of unconventional and portable devices, such as electrochemical and resistive sensors, which can be placed in locations of interest and whereas the conventional network of air quality stations is not present or cannot be representative of the area (Ragazzi et al., 2013b). The technological progress achieved during the last decade has contributed to the development of accurate sensors, whose price is becoming more and more accessible (Ragazzi et al., 2013b). In addition, electrochemical and resistive sensors can be easily integrated in wireless networks, which would allow for the transmission and storage of big amount of data and for a real-time estimate of the concentrations over a wide area.

However, although such sensors would be very useful to monitor local situations of exposure to high level of pollution (*e.g.*, peaks of concentration), significant efforts are required to lower the limit of detection of these instruments and increase their resolution. Thus, although this approach would turn useful to monitor situations of acute exposure, it is still not adequate to monitor situations of long-term exposure to low concentrations. Consequently, the hidden risk represented by contaminants that may provoke adverse effects on health over the years (*e.g.*, carcinogenic pollutants) cannot be kept under control with this approach.

The most convenient way to perform long-term air quality monitoring campaigns, with increasing the spatial resolution of the conventional networks of fixed stations, still consists in the adoption of passive sampling techniques, with following analysis in laboratory. The European legislation officially considers this method as an option to integrate the conventional approach (European Union, 2008). Passive samplers have been recently adopted also for VOC monitoring, in indoor environments (Scheepers et al., 2010; Colman Lerner et al., 2012; Król et al., 2014) or outdoors, either in remote areas (Villanueva et al., 2014) or to monitor areas in the proximity of specific emission sources (Karakitsios et al., 2007a; Lan and Binh, 2012), or to cover wide areas and retrieve fields of concentrations (Chung et al., 2009; Costabile et al., 2006).

Dispersion models, especially if coupled with risk indicators, turns particularly useful for three main purposes: firstly, if the models are calibrated with on-field measurements, reliable information on the air pollutant concentrations can be obtained by the model output, also in areas not covered by the networks of fixed air quality stations; the higher spatial representativeness of concentration maps, especially if high-resolution grids are adopted, can also provide environmental assessors and decision makers with indications on the possibility of re-locating air quality stations in more critical areas and on the need for deepening the monitoring activity with measurement campaigns (*e.g.*, by means of passive samplers); finally, in addition to being a supporting tool for urban and environmental planning, dispersion modelling allows evaluating the preferable APC technologies to be adopted by industrial activities, since atmospheric dispersion plays a fundamental role in the impacts of any emission source to its vicinity[7]. Nevertheless, dispersion models have to be intended not as an alternative to measurements, but as an integrative tool supporting the usual monitoring activity. The results of model simulations are obviously depending on the accuracy of the emission factors adopted. For instance, in the case of road traffic, a recent comparison between the emission factors of PM_{10} proposed by COPERT 4 (EMISIA, 2014) and the emission factors proposed by the emission model iMONITRAF (iMONITRAF, 2014) revealed incongruities in the calculation of the emission factors, since iMonitraf tends to overestimate the emission of PM_{10} (Stroe et al., 2014); in addition, particular care should be taken when deciding about the adoption of a steady-state model (*e.g.*, COPERT 4) or an unsteady-state model using driving cycles, like ARTEMIS (Assessment and Reliability of Transport Emission Models and Inventory Systems).

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[7] Two dispersion modeling activities, also concerning benzene, will be presented at Section 3.5 (Schiavon et al., 2015a) and Section 5.3 (Schiavon et al., 2015b).

3 Proposals for integrative methodologies for exposure assessment and environmental monitoring

3.1 Summary

This chapter moves from the considerations expressed in Chapter 2 on the need for integrative methodologies for exposure assessment and environmental monitoring. Four methodologies will be here presented, aiming at providing risk assessors with additional tools offering different features: quick identification of criticalities in terms of exposure, detection of the dominant emission source in an area, evaluation of possible strategies to improve air quality. Unconventional monitoring approaches and modelling activities are here presented as extracts from four publications carried out during this doctoral research.

The methodologies presented in Sections 3.2, 3.3 and 3.4 were elaborated on the case study of a secondary steel plant located in an Alpine valley in northern Italy. The valley is east-west oriented. On annual average, the dominant wind direction follows the orientation of the valley, although no prevalent way (E-W or W-E) is observed. The steel plant, which has been in operation since 1978, produces secondary steel from metal scraps with an electric arc furnace and has a maximal production capacity of 800,000 t y^{-1} (Schiavon et al., 2013). In 2009 the plant adopted the BATs for the abatement of polluting emissions: from the design flow of 1,350,000 Nm^3 h^{-1}, primary and secondary emissions pass through a cyclone and a bag filter; primary emissions are also subsequently cooled in a quenching tower (Schiavon et al., 2013). Near the plant, small villages, fields and some pastures are present.

The methodology presented in Section 3.5 was tested on the case study of an urban area of Verona (Italy). In addition to benzene (mainly emitted from road traffic), NO_x were chosen as model pollutants to estimate the impacts of the main urban emission sources (road traffic and domestic heating) within the urban morphology and, especially, within urban street canyons. Although non-carcinogenic compounds were excluded from this doctoral thesis, NO_x were chosen as an indicator of combustion processes, which, depending on the fuel used, may also induce cancer through the emission of carcinogenic compounds (*e.g.*, PAHs, PCDD/Fs). In this specific research, NO_x become an example of pollutants emitted from different kinds of sources whose contribution overlaps in an urban environment; the choice of such ubiquitous and common pollutants was made to point out the importance of a complete characterization of the emissive contributions in an urban environment, which determine the urban air quality. On the other hand, dispersion simulations of benzene allow evaluating the cancer risk in an urban area and detecting the presence of local critical situations of exposure that may elude the monitoring activity carried out by conventional air quality stations.

3.2 Sewage sludge characterization as a tool to detect potential anomalous situations of exposure to POPs

Based on: Rada, E.C., Schiavon, M., Ragazzi, M., 2013. Seeking potential anomalous levels of exposure to PCDD/Fs and PCBs through sewage sludge characterization. *Journal of Bioremediation & Biodegradation* 4, 210. The final publication is available at OMICS International via http://dx.doi.org/10.4172/2155-6199.1000210.

3.2.1 Introduction

The absorption of PCDD/Fs and PCBs from the diet can result higher than 80% in situations of elevated POP intake (Moser and Mclachlan, 2001). The absorption is followed by excretion from the body, which does not depend on the fluctuations of the POP intake through diet, but only on the POP concentration in the body: in fact, faecal elimination occurs continuously at a rate that depends on the POP concentration in blood (Moser and Mclachlan, 2001). The body, thus, seems to be able to equalize the effects of peaks of POP intake. After entering the human body and leaving the organism by excretion, POPs reach WWTPs and concentrate in sewage sludge. Sludge contamination is then object of great concern, if the reuse of sewage sludge in agriculture is an option (Olofsson et al., 2013). An important study focused on the mass balance of POPs throughout the human body (Moser and Mclachlan, 2001), showing the significant role of bioaccumulation.

The presence of organic (McLachlan et al., 1996; Torretta, 2012) and inorganic (Jamali et al., 2009; Smith, 2009) hazardous substances in sewage sludge has been object of investigation in several studies. Sewage sludge has also been studied as a potential source of energy (Balgaranova, 2003; Havukainen et al., 2012; Zhai et al., 2013) and as a raw material for conventional (Ingelmo et al., 1998) and non-conventional products (Tay et al., 2001). In addition to these applications, sewage sludge can be also used as a source of information to seek potential anomalous levels of exposure of a population to POPs: indeed, the dominant exposure route of POPs released by the most important sources (*e.g.*, steel plants) is the emission into the atmosphere, the atmospheric deposition to farmlands and pastures, the consequent contamination of the food produced, the intake by humans, the excretion, the transportation to WWTPs and the POP concentration in sewage sludge; thus, analyses on the POP content of sludge samples offer an alternative, inexpensive and technically simple approach to assess the existence of critical situations of exposure to POPs. Several studies focused on the ambient air and deposition monitoring in areas where steel plants were present and highlighted their evident influence in terms of PCDD/F contribution in the surroundings (Li et al., 2010; Fang et al., 2011; Onofrio et al., 2011). The present study is then intended to propose a methodology, in order to detect anomalies throughout the food chain, as a consequence of the release of POPs in air from significant sources and their subsequent deposition to farmlands and pastures.

This study focuses on a steel plant located in a west-east oriented Alpine valley in the north of Italy. In addition to represent one of the most important source of PCDD/Fs at a European level (Quaß et al., 2004), the metal sector is also an important emission source of PCBs, as demonstrated by a study on scrap metal recycling plants, whose wastewater showed a maximal dioxin-like PCB concentration of 3.61 ng I-TEQ L^{-1}

(Van Ham et al., 2011). Three domestic WWTPs, located outside the area of influence of the plant, were chosen as background reference for assessing the content of POPs in their sewage sludge. Another domestic WWTP, which receives the wastewater from the villages located in the vicinity of the steel plant, was chosen as representative of the population exposed to the intake of POPs released by the mill. One sewage sludge sample was taken from each WWTP. The samples were analysed and the results are discussed, in order to understand the potentialities of this methodology in assessing the presence of critical levels of exposure to POPs. In addition, a sensitivity analysis of the method is presented and the results are interpreted by moving from the considerations reported in Moser and Mclachlan (2001) and from the findings of a previous study, which reported that a permanent exposure to normal levels of PCDD/Fs, following a higher exposure in the past, can produce a PCDD/F excretion that is twice higher than the intake (Schrey et al., 1998). Considered the limited number of samples, the application of this approach to a specific case study has the purpose of explaining how this methodology can be applied in different contexts, with a sufficient number of samples to perform a statistical analysis and better interpret the results.

3.2.2 Material and methods

The choice of the WWTP taken as a reference for the potentially exposed population started from previous dispersion simulations of PM emitted by the plant, whose results allowed the detection of the population potentially exposed to contamination, through direct inhalation and assumption via food intake after deposition (Rada et al., 2012a). The input of the WWTP influenced by the steel plant is composed of two contributions: 75% comes by the wastewater from the potentially exposed population (about 12,670 inhabitants), while the remaining 25% comes from the wastewater of other residential unexposed populations (Authonomous Province of Trento, 2013); in addition, the wastewater treatment line receives liquid streams from the thermal drying of the provincial sewage sludge that can be supposed poor of dioxin. In fact, the liquid streams are dominated by the liquid phase, unlike domestic wastewater that has a higher content of suspended solids (or organic matter): indeed, a positive association between dioxin levels and suspended solids was found in a previous study, which supports the theory that dioxin-like compounds will partition almost exclusively onto the organic matter in sludge in preference to water (Telliard et al., 1990).

As a term of comparison, the three additional WWTPs were chosen as representative of the population living outside the study area (about 39,690 inhabitants), hence providing background information on the PCDD/F and PCB levels in the food chain. Similarly, these three plants were chosen so that their catchment areas include villages located outside the area of influence of the plant and far from significant emitters. The consultation of the local emission inventory excluded the presence of other important sources of POPs. The locations of the WWTPs and their distances from the steel plant are presented in Figure 3.1.

All the WWTPs here considered are equipped with an oxidation stage and a secondary sedimentation tank; the sludge is then conditioned with the addition of polyelectrolytes and is sent to mechanical dehydration. The choice of taking sludge samples instead of wastewater samples is related to the fact that POPs are more concentrated in sludge than in water.

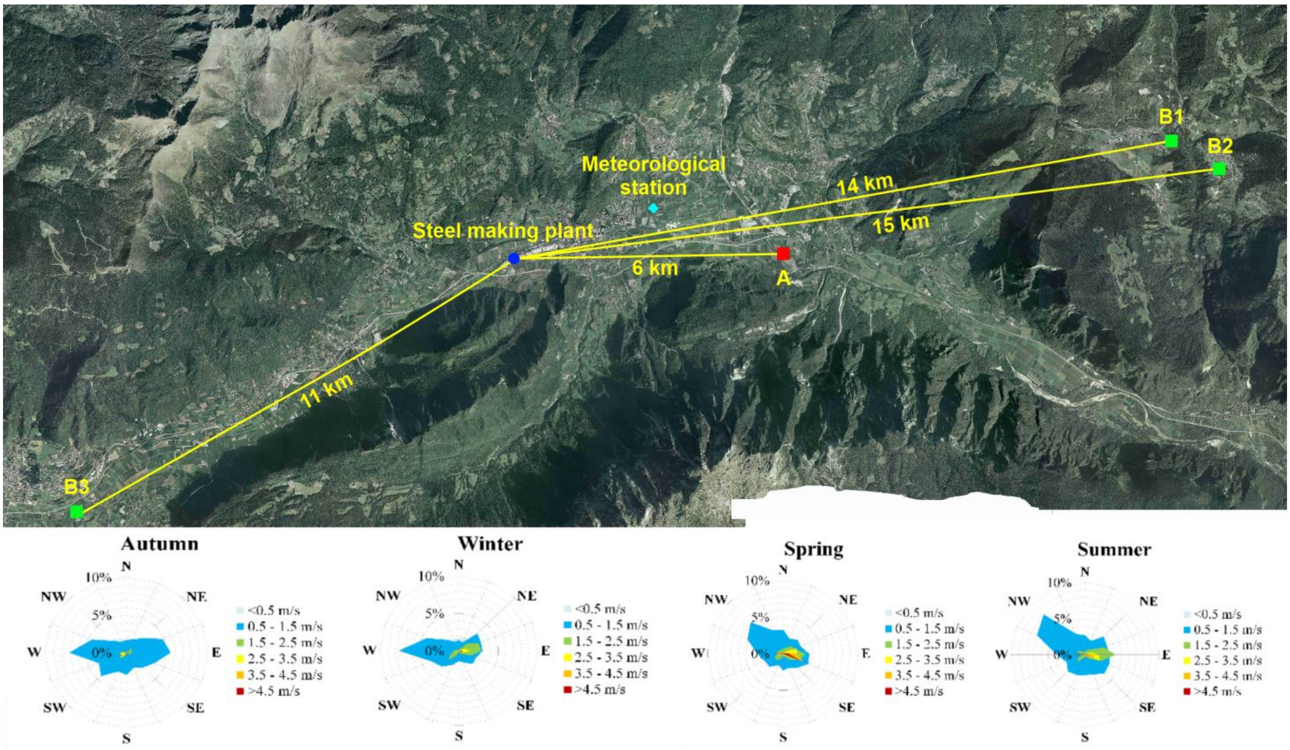

Figure 3.1: Seasonal wind roses for the case study and locations of the steel plant (blue circle), the meteorological station (light blue rhombus), the steel plant-influenced WWTP (red square), the three background WWTPs (green squares) and their respective distances from the steel plant.

As a matter of fact, the activated sludge treatment that is applied to WWTPs removes hydrophobic compounds like PCDD/Fs and PCBs from the wastewater by sorption to sludge (Ju et al., 2007). The four sewage sludge samples (sample volume of 2 L each), one for the steel plant-influenced WWTP and three for the background WWTPs, were taken and analysed before the beginning of this doctoral research, on the 12.12.2011, between 9 am and 11 am. The choice of this period of the year is crucial and is due to the need of avoiding contributions from tourist peaks in the region, which usually occur during summer or during Christmas holidays. In fact, by taking the sludge samples during the low season, only the contribution of the resident population is counted. If the sampling had been carried out during a tourist period, the results would have shown the diluting effect of a differently exposed foreign population. Since POP levels in sewage sludge change slowly, due to the slowness of the process of accumulation in the food chain, the number of samples taken at each plant is not influent on the characterization of the population exposure in a specific period (tourist periods excluded). On the other hand, primary importance should be given to the choice of the WWTPs that must be representative of the exposed and the unexposed population and must clearly distinguish between them. The four sludge samples were taken before the chemical conditioning with polyelectrolytes. Since polyelectrolytes are synthesis products, the possibility exists that such substances may contain dioxin compounds, and thus, they may increase the dioxin content of the unconditioned sludge. The choice of sampling sewage sludge before conditioning gives the certainty that no additional sources of dioxin (other than anthropic input) influenced the sludge samplings. Furthermore, cross-contamination was prevented by the adoption of glass vases as containers for the samples. Hence, the only possible source of dioxin and dioxin-like compounds could be represented by the indoor air, whose quality is kept under control and possible dioxin levels are anyway negligible if compared with the concentration in the samples.

The moisture of the samples was detected by calculation of the dry residual mass after evaporation at 105 °C, according to the EN 14346:2007 method (UNI - Italian Standards Institute, 2006). The content of PCDD/Fs was measured in accordance with the US EPA 1613 and US EPA 1668B methods (US EPA, 1994, 2008).

3.2.3 Results and discussion

The results of the analysis on the sludge samples from the WWTP taken as reference for the population potentially exposed to contamination (A) and from the three background WWTPs (B1, B2 and B3) are presented in Table 3.1 and Table 3.2, for PCDD/Fs and PCBs respectively. For some PCDD/F congeners (*e.g.*, 2,3,7,8-TCDD and 1,2,3,7,8,9-HxCDF), the concentration measured in sewage sludge is lower than the instrumental detection limit (DL) in all the WWTPs considered. Conventionally, concentrations below the DL are assumed as half the DL itself. As the results show, the total PCDD/F concentrations measured at the reference WWTP (A) are slightly higher than those measured elsewhere, since the congeners 1,2,3,4,6,7,8-HpCDD and OCDD are predominant. Moreover, such compounds are two of the most important congeners that characterize the emissions from an electric arc furnace (Zou et al., 2012), which is the technology adopted by the steel plant under investigation. On the other hand, in terms of total WHO-TEQ concentrations, the A plant shows the lowest PCDD/F content with respect to the others. Considering that the WHO-TEQ con-

Table 3.1: PCDD/F concentrations and respective WHO-TEQ concentrations in the sludge samples for the WWTP taken as reference for the population exposed to POP contamination (A) and for the background WWTPs (B1, B2 and B3).

Congener	**WHO-TEF**	**DL** [ng kg^{-1} $_{DM}$]	**Concentration** [ng kg^{-1} $_{DM}$]				**WHO-TEQ Concentration** [ng WHO-TEQ kg^{-1}$_{DM}$]			
			A	B1	B2	B3	A	B1	B2	B3
2,3,7,8-TCDD	1	0.1	<DL	<DL	<DL	<DL	0.050	0.050	0.050	0.050
1,2,3,7,8-PCDD	1	0.5	<DL	0.60	<DL	<DL	0.250	0.600	0.250	0.250
1,2,3,4,7,8-HxCDD	0.1	0.5	<DL	<DL	0.60	<DL	0.025	0.025	0.060	0.025
1,2,3,6,7,8-HxCDD	0.1	0.5	2.60	1.10	4.00	<DL	0.260	0.110	0.400	0.025
1,2,3,7,8,9-HxCDD	0.1	0.5	<DL	<DL	1.20	1.70	0.025	0.025	0.120	0.170
1,2,3,4,6,7,8-HpCDD	0.01	0.5	57.00	31.00	46.00	48.00	0.570	0.310	0.460	0.480
OCDD	0.0001	0.5	466.00	323.00	355.00	412.00	0.047	0.032	0.036	0.041
2,3,7,8-TCDF	0.1	0.5	4.10	1.60	2.40	3.30	0.410	0.160	0.240	0.330
1,2,3,7,8-PCDF	0.05	0.5	0.80	0.60	0.60	0.90	0.040	0.030	0.030	0.045
2,3,4,7,8-PCDF	0.5	0.5	<DL	0.50	1.70	1.70	0.125	0.250	0.850	0.850
1,2,3,4,7,8-HxCDF	0.1	0.5	<DL	0.70	1.40	1.60	0.025	0.070	0.140	0.160
1,2,3,6,7,8-HxCDF	0.1	0.5	0.80	1.70	0.90	1.00	0.080	0.170	0.090	0.100
2,3,4,6,7,8-HxCDF	0.1	0.5	0.60	1.60	2.00	<DL	0.060	0.160	0.200	0.025
1,2,3,7,8,9-HxCDF	0.1	0.5	<DL	<DL	<DL	<DL	0.025	0.025	0.025	0.025
1,2,3,4,6,7,8-HpCDF	0.01	0.5	17.90	16.70	6.20	16.40	0.179	0.167	0.062	0.164
1,2,3,4,7,8,9-HpCDF	0.01	0.5	<DL	0.50	0.60	<DL	0.003	0.005	0.006	0.003
OCDF	0.0001	0.5	44.00	49.00	59.00	52.00	0.004	0.005	0.006	0.005
TOTAL	-	-	595.60	429.40	482.15	540.15	2.178	2.194	3.024	2.748

Table 3.2: PCB concentrations and respective WHO-TEQ concentrations in sludge samples for the WWTP taken as reference for the population exposed to POP contamination (A) and for the background WWTPs (B1, B2 and B3).

Congener	**WHO-TEF**	**DL** [ng kg^{-1} $_{\mathrm{DM}}$]	**Concentration** [ng kg^{-1} $_{\mathrm{DM}}$]				**WHO-TEQ Concentration** [ng WHO-TEQ kg^{-1} $_{\mathrm{DM}}$]			
			A	B1	B2	B3	A	B1	B2	B3
PCB 77	0.0001	1	492.0	71.0	172.0	191.0	0.0492	0.0071	0.0172	0.0191
PCB 81	0.0003	1	19.6	<DL	1.4	1.9	0.0059	0.0002	0.0004	0.0006
PCB 105	0.00003	1	1890.0	233.0	650.0	700.0	0.0567	0.0070	0.0195	0.0210
PCB 114	0.00003	1	162.0	<DL	48.0	59.0	0.0049	0	0.0014	0.0018
PCB 118	0.00003	1	5210.0	1290.0	1800.0	1800.0	0.1563	0.0387	0.0540	0.0540
PCB 123	0.00003	1	403.0	35.0	136.0	126.0	0.0121	0.0011	0.0041	0.0038
PCB 126	0.1	1	5.2	<DL	1.4	7.1	0.5200	0.0500	0.1400	0.7100
PCB 156	0.00003	1	600.0	151.0	343.0	343.0	0.0180	0.0045	0.0103	0.0103
PCB 157	0.00003	1	99.0	32.0	67.0	52.0	0.0030	0.0010	0.0020	0.0016
PCB 167	0.00003	1	141.0	55.0	97.0	114.0	0.0042	0.0017	0.0029	0.0034
PCB 169	0.03	1	7.0	2.1	2.8	6.4	0.2100	0.0630	0.0840	0.1920
PCB 189	0.00003	1	53.0	14.0	20.0	18.8	0.0016	0.0004	0.0006	0.0006
TOTAL	-	-	9081.8	1884.6	3338.6	3419.2	1.0418	0.1746	0.3365	1.0181

centrations are related to the toxicity for humans, no anomalies in PCDD/Fs were detected in the food chain for the potentially exposed population. These results are in agreement with the fact that the PCDD/F deposition in the surroundings of the steel plant, in terms of WHO-TEQ values, is substantially low and can be considered as similar to that normally found in rural areas (Schiavon et al., 2013). The use of wood as a source for domestic heating, which is typical of mountainous regions where this material is abundant, may have had a certain influence in making the results of the four samples comparable. The PCDD/F concentrations found in the samples are within the range 1.2-15.3 ng WHO-TEQ $\mathrm{kg}^{-1}_{\mathrm{dw}}$ measured in a previous study on Australian WWTPs (Clarke et al., 2008) and are lower than the average concentrations found in two German WWTPs, expressed in terms of I-TEQ concentrations (25 and 10 ng I-TEQ $\mathrm{kg}^{-1}_{\mathrm{dw}}$) (McLachlan et al., 1996).

With regards to PCB concentrations, some considerations that slightly differ from the case of PCDD/Fs can be made: the total concentration in the A plant is between 2.7- and 4.8-time higher than the other plants. The same sludge sample shows a WHO-TEQ concentration that is higher than the B1 and B2 samples, but is similar to the B3 sample, where the concentration of the most toxic congener (PCB 126) is also higher. The different urbanization, compared to the B1 and B2 plants, can explain this aspect, since the B3 case is characterized by a moderate presence of small craft activities.

Some considerations about the sensitivity of the methodology can also be expressed. If considering that 75% of the stream is composed by wastewater from the exposed population, the ratio between the POP concentrations visible in the sewage sludge after and before the increase in exposure (ΔPOP_{sludge}) can be calculated by the following equation:

$$\Delta POP_{sludge} = 0.75 \Delta POP_{faeces} + 0.25 \Delta POP_{other} \qquad \text{Eq. 3.1}$$

where ΔPOP_{faeces} is the ratio between the POP concentration in the faeces after and before the increase in exposure and ΔPOP_{other} is the ratio between the POP concentration in the sludge from the unexposed population whose wastewater is collected at plant A after and before the increase in the exposure of the target population.

In conditions of permanent exposure, ΔPOP_{faeces} is considered as equal to the ratio between the intakes by the human body after and before the exposure increase (ΔPOP_{in}) (Moser and Mclachlan, 2001), which is the sum of the ratios between the POP concentration in the locally produced food ($\Delta POP_{food,loc}$), the POP concentration in the non-locally produced food ($\Delta POP_{food,nloc}$) and in air (ΔPOP_{air}), after and before the exposure increase:

$$\Delta POP_{faeces} = \Delta POP_{in} = C_{food,loc} I_{POP,food} \Delta POP_{food,loc} + C_{food,nloc} I_{POP,food} \Delta POP_{food,nloc} + I_{POP,inhal} \Delta POP_{air} \qquad \text{Eq. 3.2}$$

where $C_{food,loc}$ is the percentage of the consumption of locally produced food on the total diet, $C_{food,nloc}$ is the percentage of the consumption of non-locally produced food, $I_{POP,food}$ is the percentage of POPs taken in by food consumption, the remaining part being attributed to the intake of POPs by inhalation ($I_{POP,inhal}$). $C_{food,loc}$ is assumed as equal to 10% of the total food consumed by the local population, in accordance with a previous study (Cernuschi, 2003). This assumption is reasonable, since several cultivated fields, cattle and dairy farms are located in the area surrounding the steel plant and support the local economy. consequently, $C_{food,nloc}$ is equal to 90%; following the findings of Eduljee and Gair (1996), $I_{POP,food}$ is assumed equal to 90%, and consequently, $I_{POP,inhal}$ is equal to 10%. If considering ΔPOP_{in} only addressed to the consumption of local food, $\Delta POP_{food,nloc}$ and ΔPOP_{air} are equal to 1. Thus, by applying Eq. 3.2, a 100-fold increase of concentration in the locally produced food ($\Delta POP_{food,loc}$ = 100) would result in an increase of 9.91 times in the POP content in feces (ΔPOP_{faeces} = 9.91). If assuming the POP concentration in the sludge from the unexposed population whose wastewater is collected at plant A as unvaried (ΔPOP_{other} = 1), by applying Eq. 3.1, a 7.7-time higher concentration should be observed in the sewage sludge at the steel plant-influenced WWTP.

In this specific case study, the assumption of permanent exposure cannot be made, since in 2009, the steel plant significantly modified the off-gas treatment line in order to decrease its emissions. In this case, the sensitivity of the method can be assessed by considering that, in conditions of permanent exposure to normal levels following a higher exposure in the past, the PCDD/F excretion can result twice higher than the intake (Schrey et al., 1998). In this case, $\Delta POP_{faeces} = 2\Delta POP_{in}$, and if considering a past concentration in the locally produced food that was 100-time higher than the background ($\Delta POP_{food,loc}$ = 100), ΔPOP_{sludge} would be approximately equal to 15. It should be taken into account that the 2.7-4.8 time higher PCB concentrations found at the A plant can be also explained by the higher exposure that occurred in the past.

On the other hand, this method is not able to detect acute episodes of exposure, since, as previously stated, in such situations even only 20% of the assumed POPs can be excreted (Moser and Mclachlan, 2001): in this case, $\Delta POP_{faeces} = 0.2\Delta POP_{in}$ and ΔPOP_{sludge} would become comparable with that one achievable in permanent conditions if the concentration in the locally produced food was 12-time higher than the background, thus giving misleading results.

Given that the contribution of food consumption in the intake of POPs is dominant and assuming as acceptable the daily intake of the population living in the areas B1, B2 and B3 (for the absence of significant sources of POPs), the fact that the concentrations of POPs in the sewage sludge at the A plant are similar to those found in the unexposed areas allows excluding the presence of a dioxin and dioxin-like emergency in the area of the steel plant, even if the presence of the steel plant is visible by the detection of some congeners characteristic of the emissions from electric arc furnaces. These positive results can be attributed also to the technology adopted, as the arc furnace has a less impact in terms of dioxin emissions with respect to other technologies (Quaß et al., 2004).

Possible wastewater contaminations can derive from surface runoff, but this contribution was found to be limited to about 10% in a previous work (McLachlan et al., 1996). Laundry washing is an additional source of PCDD/Fs, and its contribution can be comparable with the one of domestic wastewater (McLachlan et al., 1996). However, if considering the habits unchanged over the years, the contribution of laundry washing can be considered constant; thus, a hypothetical 100-time higher dietary exposure would be anyway visible in terms of POP concentration in sludge.

3.2.4 Conclusions

A novel, inexpensive and technically simple methodology to detect anomalies in the exposure to POPs throughout the food chain was presented. This methodology, suitable also for preventing soil contamination, was applied to the case of a steel plant and the residential population living in the surroundings, but the approach can be applied to any case where a population is exposed to contamination by POPs. Given the limited number of samples, the application to the present case study has the purpose of better explaining how the methodology works, without providing definitive results on the exposure assessment of the target population. For future applications and for a better reliability and solidity of the method, increasing the number of samples at every WWTP is necessary. Three samplings under the same conditions at each site will allow a statistical analysis of the results. However, considering acceptable the daily intake from the diet of the population living in the areas not affected by the steel plant, the absence of a dioxin and dioxin-like emergency in the area of the steel plant can be deducted by the similar concentrations of PCDD/Fs and PCBs in the sewage sludge samples.

This method is able to assesses situations of long period exposure of the population to POP levels that are higher than the background, even if difficulties in the interpretation of the results can occur in presence of acute episodes.

3.3 Assessment of the local role of a steel plant by measuring depositions of POPs

Based on: Rada, E.C., Ragazzi, M., Schiavon, M., 2014. Assessment of the local role of a steel making plant by POPs deposition measurements. *Chemosphere* 110(1), 53-61. The final publication is available at Elsevier via http://dx.doi.org/doi:10.1016/j.chemosphere.2014.03.024.

3.3.1 Introduction

As mentioned at Section 2.3.1.8, one of the main contributor of PCDD/Fs in Europe is the sector of the steel and sintering plants. Contributions derive also from the waste sector (*e.g.*, mechanical-biological treatments and incineration) and the combustion of biomass (Pieper et al., 2002; Rada and Ragazzi, 2008; Rada et al., 2007, 2006; Vehlow, 2012; Lundin et al., 2013) with diffuse emissions that have been pointed out recently as an underestimated phenomenon (Rada et al., 2011). In addition to PCDD/Fs, the dioxin-like PCBs were recently classified as known carcinogens for humans: dioxin-like PCBs, similarly to PCDD/Fs, can accumulate into the food chain and induce melanoma; positive associations for breast cancer and non-Hodgkin lymphoma were also observed (IARC, 2015b).

With regards to the steel sector, the conveyed gas does not represent the only emissive contribution. Secondary emissions, diffuse emissions from slag deposits and leaks from the air treatment systems are additional sources and are subject to different dispersion processes into the atmosphere. Recent studies aimed at assessing the impacts of steel plants on the surrounding areas, mainly focusing on their contribution to the ambient air concentration of PCDD/Fs and dioxin-like compounds (Li et al., 2010; Onofrio et al., 2011). Since about 90% of the PCDD/F intake is attributable to ingestion of contaminated food, the atmospheric deposition to soil is an important phenomenon to be monitored (Rada et al., 2011; Vassura et al., 2011).

In order to further investigate the influence of the steel plant presented at Section 3.1, a monitoring campaign on atmospheric deposition was activated in 2010, in the Alpine valley object of study. The valley is also characterized by the presence of cultivated lands and farms. Three deposimeters were placed in the area surrounding the plant, depending on the purpose of each specific monitoring activity (*e.g.*, impact on sensitive receptors, influence of primary and diffuse emissions). The results were interpreted and discussed in 2013, at the beginning of this doctoral research.

3.3.2 Material and methods

To monitor the atmospheric deposition of PCDD/Fs, Depobulk® deposimeters were adopted. Each deposimeter consists of a funnel coupled with a jar (both made of Pyrex® glass) that collects wet and dry deposition together (Schiavon et al., 2013). The funnel/jar combination allows for the collection of settling particles and wet depositions, with the contribution from dry gaseous depositions and impacting/diffusing particles (Horstmann and McLachlan, 1997). Each deposimeter is equipped with a special ring to avoid interferences from bird excreta. This tool allows collecting the total deposition contribution from the atmosphere for a period of about 15-30 days, after which the deposimeter is analysed and regenerated for the following sampling period. Bulk deposition samplers mainly collect the particle phase of the compounds depositing to soil and an increase in the proportion of particle-bound PCDD/Fs with increasing distance from the dominant source was observed in a previous study (Chao et al., 2004). Thus, deposimeters can be adopted as an effective method to monitor the influence of industrial activities not only in the vicinity of the plants.

The monitoring campaign started with the choice of the most important site to be monitored: by crossing the information deriving from a previous simulation of dispersion (Rada et al., 2012a) with the population density of the area and the presence of sensitive receptors, a school building (a primary school coupled with a kindergarten) located in the village near the plant was selected as the primary sampling site (site 1). The school building (site 1) is about 1.2 km far from the steel plant, is located between the latter and the center of the village and is frequently downwind from the plant (Figure 3.2). The sampling period at site 1 covered 13 months (from August 2010 to September 2011).

To better investigate the potential influence of the steel plant, a second site (site 2) was selected between the plant and site 1, in accordance with the results of the dispersion simulations that pointed out a potential high deposition in the proximity of the plant due to diffuse emissions. The sampling period at site 2 covered 12 months (from April 2011 to April 2012).

A slag deposit is present just outside the main building of the plant. The slag coming from the steel-making process is cooled, with potential stripping of POPs. In order to mainly study the influence of diffuse emissions coming from the slag deposit, a third sampling site (site 3) was selected near the kindergarten of a village located about 2 km west from the plant, on the side of the deposit, and frequently downwind from it. The sampling period at site 3 covered 6 months and was carried out between October 2011 and March 2012.

In addition to PCDD/Fs, all the samples were analysed for PCBs and PAHs, in order both to evaluate possible anomalies from such compounds and to detect the presence of other emission sources that could interfere with the release of PCDD/Fs from the steel plant.

The steel plant operated from 8 p.m. to 8 a.m. on weekly days and 24 h d^{-1} during the weekend, for rea-

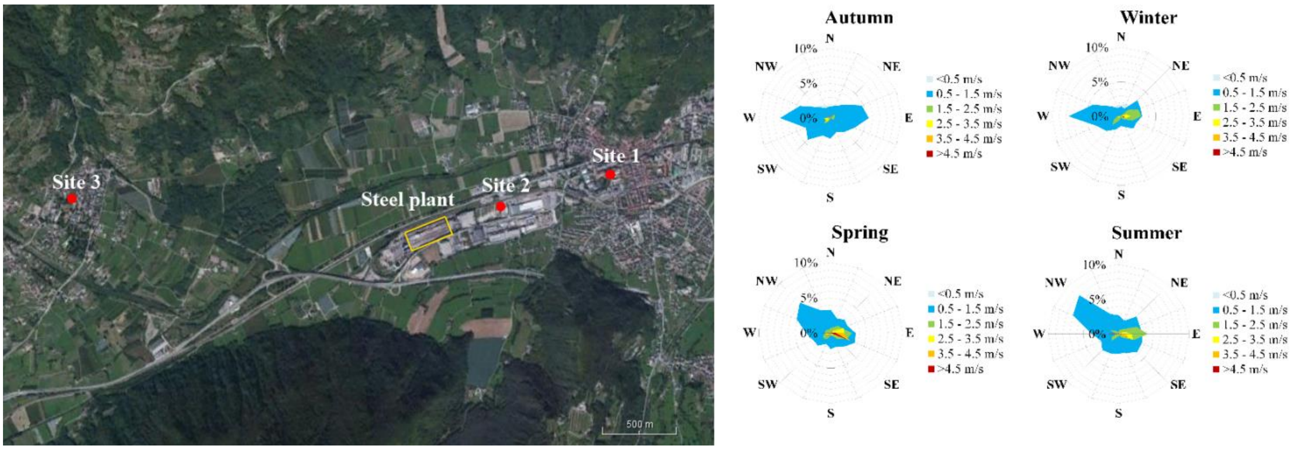

Figure 3.2: Location of the steel plant and the three sampling sites and detail of the seasonal wind roses for the area under investigation.

sons related to the cost of energy. Generally, the plant stops twice a year: in the middle of summer and for Christmas holidays. In order to clearly characterize the operative and non-operative periods, the cleaning and the regeneration of the deposimeters were synchronized with the calendar of the activities. Rainy and snowy periods and temperature were taken under observation thanks to a meteorological station located nearby, in order to replace the deposimeters before the possible overflow of the collected water and to prevent damages from ice formation. PCDD/Fs and PCBs were analysed in laboratory in accordance with the US EPA Methods 1613 and 1668B (US EPA, 1994, 2008), respectively. In the absence of specifications about the high resolution analysis of PAHs in the current legislation, such compounds were extracted with pure hexane and the solution was purified on a silica gel column. PCDD/Fs and PCBs were extracted from the aqueous matrix with a mixture acetone-hexane. The solutions with PCDD/Fs and PCBs were then purified on a mixed chromatographic column. The three families of pollutants were then analysed by high resolution gas chromatography and mass spectrometry (HRGC/HRMS). The mass of pollutants measured in each sample was divided by the surface of the deposimeter (0.0346 m^2) and by the period of characterization, to obtain the deposition values.

3.3.3 Results and discussion

The total PCDD/F deposition measured at site 1 over the 13 months of sampling shows a high variability (Table 3.3). Largely, higher values were achieved during winter and the lowest values were measured during spring and summer. This behaviour can be explained by differences in the dilution process between winter and summer: the plant is located in a narrow valley where conditions of atmospheric stability often occur during winter. As a consequence, the pollutants tend to be trapped at the valley bottom. In addition, wood burning for domestic heating is a common practice in the Alpine region and contributes to the emissions of PCDD/Fs (Rada et al., 2012b; European Environment Agency, 2013). In secondary steel plants, PCDD/F emissions are mainly generated by already existing POPs in the raw material (McKay, 2002; Odabasi et al., 2010; Tian et al., 2012); PCDD/Fs can also undergo *de novo* synthesis by reaction with chlorine, carbon, oxygen and hydrogen, causing the formation of precursors (Environment Australia, 1999). Moreover, the PCDD/F generation can be catalysed by metals involved in the steel production process (Zou et al., 2012).

To investigate the role of the steel plant more in details, in April 2011 the monitoring of the atmospheric deposition was started at site 2. As expected, higher PCDD/F depositions were found in comparison with those measured at site 1, with exceptions for the two anomalous samples collected during the periods 29 June – 8 August and 8 September – 3 October 2011: in these cases, the depositions at site 1 were higher than those measured at site 2. The maximal PCDD/F deposition at site 2 (9.46 pg I-TEQ m^{-2} d^{-1}) was measured during the period 12 January – 22 February 2012 (Table 3.3). No clear annual variability can be detected, although the deposition achieved its minimum (0.57 pg I-TEQ m^{-2} d^{-1}) during summer holidays, when the plant was stopped.

Table 3.3: Atmospheric bulk deposition of PCDD/Fs measured at the three sampling sites during the monitoring campaign.

Sampling period	**PCDD/F total deposition [pg m^{-2} d^{-1}]**		
	site 1	site 2	site 3
9 Aug 2010 30 Aug 2010*	0.83	-	-
31 Aug 2010 21 Sep 2010	1.63	-	-
22 Sep 2010 13 Oct 2010	2.12	-	-
14 Oct 2010 2 Nov 2010	1.71	-	-
3 Nov 2010 25 Nov 2010	2.66	-	-
24 Dec 2010 3 Jan 2011*	3.34	-	-
4 Jan 2011 14 Jan 2011	2.48	-	-
1 Feb 2011 1 Mar 2011	1.74	-	-
2 Mar 2011 5 Apr 2011	0.36	-	-
8 Apr 2011 18 May 2011	0.41	0.60	-
19 May 2011 28 Jun 2011	0.51	1.08	-
29 Jun 2011 8 Aug 2011	2.49	0.57	-
9 Aug 2011 7 Sep 2011*	0.80	3.58	-
8 Sep 2011 13 Oct 2011	3.85	1.60	28.63
14 Oct 2011 14 Nov 2011	-	0.74	0.41
15 Nov 2011 23 Dec 2011	-	0.97	16.24
24 Dec 2011 11 Jan 2012*	-	1.09	0.40
12 Jan 2012 22 Feb 2012	-	9.46	121.95
23 Feb 2012 20 Mar 2012	-	1.63	1.23
21 Mar 2012 18 Apr 2012	-	4.07	2.25

* Suspension of the activities of the steel plant

The variability in the deposition measurements is much more evident at site 3: two peaks of 28.63 and 16.24 pg I-TEQ m^{-2} d^{-1} were observed during the periods 4 October – 13 October and 15 November – 23 December 2011, respectively. During the same periods, no incongruities were found between the other organic pollutants monitored (PCBs and PAHs) at site 3 and the same compounds monitored at the other sites. Thus, such anomalies were only related to PCDD/Fs. An extremely high peak of PCDD/F deposition (121.95 pg I-TEQ m^{-2} d^{-1}) was measured during the period 12 January – 22 February 2012, when site 2 experienced the highest deposition (Table 3.3).

No anomalies were found for PCBs and PAHs during the same period, so that the PCDD/F congener distribution was studied to investigate the possible reasons for such a peak (Table 3.4, Table 3.5, Table 3.6). The congener distribution quite differs from the previous months and this could indicate a variation in the dominant source of PCDD/Fs for site 3 (Table 3.6). In addition, the congener distribution looks similar to that observed at site 2 in the same period, indicating that the same phenomenon influenced a large area.

Due to the high variability of PCDD/F depositions and since PAH depositions are also mostly uncorrelated with the other compounds analysed, it was decided to study the congener distribution of PCBs. At all the sites investigated and during the whole respective sampling periods, the distributions were similar to that found in the ash deposited in the bag filter used in the air treatment stage of the plant (Table 3.7). The electric arc furnace is contained in a so-called “dog house”, aimed at retaining the emissions and conveying them to the bag filter. This technology has anyway a limited retaining efficiency and part of the emissions leave the plant as secondary emissions.

The similarity between the deposition measurements and the PCB profile of the ash gives credit to their common origin. The role of the steel plant is further clarified by the distributions found at site 1 and site 2 during the suspension of the activities (9 August– 7 September 2011), which differ from the distributions observed in all the other periods.

With the aim of investigating the possible sources influencing the depositions at the three sites, some hypotheses were made, based on comparisons between the measured depositions and the emissive spectra of different emission sources. As a confirmation of the influence of wood burning at site 1, for instance, the highest value measured during winter 2010-2011 at this site (3.34 pg I-TEQ m^{-2} d^{-1}) occurred during the period 24 December 2010 – 3 January 2011, when the activity of the steel plant was stopped for Christmas holidays (Table 3.3). The distribution of the PCDD/F congeners measured during that period was compared to the typical distribution of the emissions from wood burning in domestic stoves, where OCDD accounts for 70-80% in mass (Pfeiffer et al., 2000; US EPA, 2006). In the flue gas, PCDD/Fs are mainly present in the gaseous phase, but in ambient air the presence of PCDD/Fs in the particle phase is dominant, being almost 100% for the congeners with high degrees of chlorination (Li et al., 2008; Lohmann et al., 2000) and this is particularly evident during winter (Kadowaki and Naitoh, 2005). Thus, sorption is the main fate for PCDD/F emissions (Chao et al., 2004). For lowly chlorinated congeners, the partitioning is dominated by the gas phase. However, in the specific case of emissions from wood combustion, TCDD/Fs and PeCDD/Fs are only 1-15% of the total PCDD/Fs; lower percentages are achieved in the deposimeters (0.01-7%), which mainly collect the particle phase. A partial comparison between the emissive fingerprint and the deposition spectrum, although being an approximation and if neglecting the less contributing congeners, can be considered as a valid approach. However, more research is needed to study the distribution of the congeners into the granulometric fractions, since lowly chlorinated congeners were found to be prevalently associated to coarse particles and highly chlorinated congeners to smaller ones (Oh et al., 2002; Shih et al., 2009).

Table 3.4: PCDD/F congener distribution observed in the deposition samples collected at site 1.

sampling period	**PCDD/F congener distribution at site 1 [%]**																
	2,3,7,8 TCDD	1,2,3,7,8 PCDD	1,2,3,4,7,8 HxCDD	1,2,3,6,7,8 HxCDD	1,2,3,7,8,9 HxCDD	1,2,3,4,6,7,8 HpCDD	OCDD	2,3,7,8 TCDF	1,2,3,7,8 PCDF	2,3,4,7,8 PCDF	1,2,3,4,7,8 HxCDF	1,2,3,6,7,8 HxCDF	2,3,4,6,7,8 HxCDF	1,2,3,7,8,9 HxCDF	1,2,3,4,6,7,8 HpCDF	1,2,3,4,7,8,9 HpCDF	OCDF
09 Aug 2010 30 Aug 2010*	0.10	0.21	1.52	1.06	0.33	7.23	17.41	9.42	2.01	3.67	6.95	4.02	7.23	1.11	24.26	13.04	0.44
31 Aug 2010 21 Sep 2010	0.03	0.92	0.06	2.78	0.04	20.75	42.61	5.50	1.31	2.28	2.16	4.75	0.09	0.04	15.19	0.97	0.53
22 Sep 2010 13 Oct 2010	0.21	0.29	0.02	0.11	0.02	10.83	45.91	9.76	3.91	4.45	3.80	3.53	4.66	0.04	9.39	0.17	2.91
14 Oct 2010 2 Nov 2010	0.03	0.03	0.07	0.06	0.08	15.28	42.62	2.14	0.03	8.98	1.98	4.16	4.77	0.05	7.67	1.10	10.96
3 Nov 2010 25 Nov 2010	0.04	0.98	0.10	1.63	0.16	13.45	45.36	2.88	0.43	3.12	2.96	6.15	2.63	0.21	8.71	1.39	9.79
24 Dec 2010 3 Jan 2011*	0.01	0.01	0.01	0.03	0.01	10.67	65.43	2.35	0.91	2.04	3.48	0.84	2.83	0.01	5.85	0.49	5.04
4 Jan 2011 14 Jan 2011	0.03	0.29	1.34	1.53	1.13	12.82	27.37	7.45	3.40	3.46	3.88	4.11	6.92	0.77	14.07	1.53	9.90
1 Feb 2011 1 Mar 2011	0.02	1.29	1.39	3.51	1.25	11.67	34.26	3.66	4.79	4.06	3.94	4.37	5.21	0.60	9.85	3.38	6.75
2 Mar 2011 5 Apr 2011	0.02	0.05	0.20	2.47	0.41	4.82	57.58	4.44	1.52	0.06	0.96	1.02	4.65	0.07	16.29	1.68	3.75
8 Apr 2011 18 May 2011	0.03	1.40	0.05	0.31	0.10	14.91	66.98	3.48	0.37	0.44	0.43	0.88	0.03	0.05	8.45	0.14	1.95
19 May 2011 28 Jun 2011	0.02	0.08	0.13	0.36	0.19	9.93	36.95	1.95	0.64	1.74	3.98	3.74	4.69	0.06	17.96	0.90	16.70
29 Jun 2011 8 Aug 2011	0.01	0.01	0.01	0.03	1.51	8.28	50.83	1.19	1.05	1.12	3.74	1.04	2.29	0.14	14.16	1.10	13.51
9 Aug 2011 7 Sep 2011*	0.09	0.10	0.02	0.39	0.14	10.69	77.87	1.82	0.23	0.71	0.57	0.22	0.69	0.07	3.53	0.44	2.41
08 Sep 2011 3 Oct 2011	0.01	0.34	0.06	0.74	0.09	3.52	30.10	1.32	2.41	7.71	6.95	4.21	4.48	0.23	16.23	2.92	18.68

* Suspension of the activities of the steel plant

Table 3.5: PCDD/F congener distribution observed in the deposition samples collected at site 2.

sampling period	**PCDD/F congener distribution at site 2 [%]**																
	2,3,7,8 TCDD	1,2,3,7,8 PCDD	1,2,3,4,7,8 HxCDD	1,2,3,6,7,8 HxCDD	1,2,3,7,8,9 HxCDD	1,2,3,4,6,7,8 HpCDD	OCDD	2,3,7,8 TCDF	1,2,3,7,8 PCDF	2,3,4,7,8 PCDF	1,2,3,4,7,8 HxCDF	1,2,3,6,7,8 HxCDF	2,3,4,6,7,8 HxCDF	1,2,3,7,8,9 HxCDF	1,2,3,4,6,7,8 HpCDF	1,2,3,4,7,8,9 HpCDF	OCDF
8 Apr 2011 18 May 2011	0.13	2.41	0.04	0.07	0.06	6.98	55.67	0.04	0.05	0.07	4.06	0.04	0.05	0.01	18.48	0.11	11.73
19 May 2011 28 Jun 2011	0.01	0.01	0.01	0.01	0.01	16.02	34.84	4.37	0.01	4.35	1.22	0.46	2.15	0.01	16.66	0.06	19.79
29 Jun 2011 8 Aug 2011	0.02	0.05	0.16	0.19	0.57	24.20	12.99	3.37	0.41	0.67	4.16	9.29	6.50	0.02	26.70	0.07	10.62
9 Aug 2011 7 Sep 2011*	0.03	0.01	0.40	1.01	0.22	10.51	24.14	0.12	0.20	0.51	1.52	2.73	4.20	0.27	21.36	4.60	28.15
8 Sep 2011 13 Oct 2011	0.62	0.25	0.10	0.41	0.14	4.74	35.15	0.58	2.66	1.22	1.97	2.50	2.82	0.68	12.97	0.15	33.02
14 Oct 2011 14 Nov 2011	0.02	0.02	0.22	0.25	0.01	9.45	61.17	0.93	1.73	1.32	1.71	1.80	0.53	0.00	6.86	0.08	13.88
15 Nov 2011 23 Dec 2011	0.02	0.02	0.02	0.29	0.05	9.99	36.93	0.40	0.42	5.60	2.54	5.18	1.46	0.09	24.94	0.15	11.92
24 Dec 2011 11 Jan 2012*	0.01	0.07	0.10	0.19	0.06	23.83	63.60	3.45	0.39	0.54	0.30	0.30	0.30	0.01	1.96	1.87	3.03
12 Jan 2012 22 Feb 2012	0.00	0.20	0.10	1.35	0.86	15.82	18.68	0.60	0.34	2.96	5.07	4.17	8.18	0.33	13.81	5.33	22.19
23 Feb 2012 20 Mar 2012	0.01	1.46	0.34	0.34	0.01	9.74	36.88	0.19	1.87	2.24	3.45	1.60	3.79	8.75	20.02	0.01	9.29
21 Mar 2012 18 Apr 2012	0.00	0.00	0.26	0.46	0.27	10.69	22.94	1.67	0.11	1.31	3.01	2.83	5.69	0.07	30.12	1.10	19.46

* Suspension of the activities of the steel plant

Table 3.6: PCDD/F congener distribution observed in the deposition samples collected at site 3.

sampling period	**PCDD/F congener distribution at site 3 [%]**																
	2,3,7,8 TCDD	1,2,3,7,8 PCDD	1,2,3,4,7,8 HxCDD	1,2,3,6,7,8 HxCDD	1,2,3,7,8,9 HxCDD	1,2,3,4,6,7,8 HpCDD	OCDD	2,3,7,8 TCDF	1,2,3,7,8 PCDF	2,3,4,7,8 PCDF	1,2,3,4,7,8 HxCDF	1,2,3,6,7,8 HxCDF	2,3,4,6,7,8 HxCDF	1,2,3,7,8,9 HxCDF	1,2,3,4,6,7,8 HpCDF	1,2,3,4,7,8,9 HpCDF	OCDF
04 Oct 2011 13 Oct 2011	0.03	1.22	0.23	1.48	0.36	16.77	25.65	0.51	2.10	2.07	4.78	4.34	4.70	0.04	26.66	2.38	6.67
14 Oct 2011 14 Nov 2011	0.02	0.00	0.04	1.16	0.21	4.21	61.99	2.90	0.45	0.07	3.60	3.17	1.31	0.07	10.07	0.03	10.68
15 Nov 2011 23 Dec 2011	0.00	0.02	0.08	1.38	0.93	26.23	63.56	0.04	0.02	0.24	0.35	0.54	1.02	0.02	2.81	0.08	2.71
24 Dec 2011 11 Jan 2012*	0.05	0.35	0.03	0.28	0.73	16.77	53.79	1.18	1.09	0.11	1.91	3.22	3.55	0.03	1.91	2.62	12.36
12 Jan 2012 22 Feb 2012	0.00	0.23	0.96	1.86	1.48	9.65	11.97	0.72	2.92	3.53	6.46	9.80	9.85	0.09	26.26	2.76	11.46
23 Feb 2012 20 Mar 2012	0.04	0.44	0.13	0.15	0.40	8.55	17.75	2.52	0.49	0.87	4.72	5.88	4.48	2.17	24.48	2.10	24.81
21 Mar 2012 18 Apr 2012	0.00	0.00	0.00	0.20	0.13	3.53	24.42	1.54	0.02	0.02	3.86	1.74	4.23	0.09	38.40	0.95	20.84

* Suspension of the activities of the steel plant

Table 3.7: PCB congener distributions observed at the three sampling sites and comparison with the average PCB congener distribution found in samples of ash prior to the dust removal of the plant.

sampling point	sampling period	PCB congener distribution [%]											
		77	81	105	114	118	123	126	156	157	167	169	189
site 1	01 Feb 2011 - 1 Mar 2011	3.72	0.09	13.46	0.19	41.97	1.75	0.09	20.36	1.98	12.04	0.62	3.72
	2 Mar 2011 - 5 Apr 2011	4.28	0.07	12.55	0.84	46.06	2.69	0.07	18.54	2.71	6.99	0.07	5.13
	08 Apr 2011 - 18 May 2011	5.29	0.05	7.22	0.28	57.99	1.77	0.15	18.21	1.48	6.51	0.05	1.00
	19 May 2011 - 28 Jun 2011	3.96	0.19	22.92	1.17	58.43	3.78	0.02	5.12	0.94	3.33	0.02	0.11
	29 Jun 2011 - 08 Aug 2011	1.93	0.04	20.54	0.04	57.07	0.25	0.04	12.47	0.22	5.27	0.10	2.02
	09 Aug 2011 - 7 Sep 2011*	0.33	0.16	0.82	0.16	67.21	0.16	0.16	28.38	0.82	0.82	0.16	0.82
	08 Sep 2011 - 3 Oct 2011	12.64	3.88	11.25	1.06	43.81	1.99	1.16	13.94	2.19	4.38	0.51	3.19
site 2	08 Apr 2011 - 18 May 2011	6.17	0.03	12.58	0.74	51.08	2.62	0.10	16.63	1.62	5.79	0.03	2.62
	19 May 2011 - 28 Jun 2011	5.08	0.09	20.93	0.41	57.74	4.22	0.02	6.67	0.69	3.02	0.02	1.12
	29 Jun 2011 - 08 Aug 2011	3.47	0.05	7.50	0.05	78.63	3.02	0.20	4.11	0.23	0.23	0.05	2.47
	09 Aug 2011 - 7 Sep 2011*	1.76	0.88	42.25	0.88	17.61	0.88	0.88	13.20	4.40	4.40	0.88	11.97
	08 Sep 2011 - 13 Oct 2011	6.64	0.06	12.56	0.80	54.58	0.60	0.17	16.54	0.30	6.40	0.06	1.29
	14 Oct 2011 - 14 Nov 2011	4.77	0.03	16.08	0.44	47.20	1.97	0.03	20.90	0.84	5.39	0.03	2.33
	15 Nov 2011 - 23 Dec 2011	3.07	0.07	19.71	0.07	53.88	0.23	0.07	16.50	1.14	4.82	0.07	0.37
	24 Dec 2011 - 11 Jan 2012*	0.75	0.08	13.98	0.08	52.51	1.46	0.08	21.30	0.41	5.53	0.08	3.74
	12 Jan 2012 - 22 Feb 2012	0.47	0.06	14.42	0.06	70.98	0.60	0.06	7.65	1.01	0.65	0.06	3.99
	23 Feb 2012 - 20 Mar 2012	2.25	0.03	6.42	0.21	63.08	1.97	0.07	15.15	0.70	5.63	0.03	4.45
	21 Mar 2012 - 18 Apr 2012	0.22	0.11	8.46	0.11	50.11	0.11	0.11	27.84	0.56	10.02	0.11	2.23
site 3	04 Oct 2011 - 13 Oct 2011	4.83	0.06	7.31	0.06	51.63	1.56	0.06	17.83	2.60	10.65	0.06	3.34
	24 Dec 2011 - 11 Jan 2012*	4.90	0.09	15.59	0.09	60.96	1.98	0.09	8.58	0.44	2.47	0.09	4.73
	12 Jan 2012 - 22 Feb 2012	0.80	0.16	6.73	0.64	48.38	0.51	0.16	25.31	0.80	12.18	0.16	4.17
	23 Feb 2012 - 20 Mar 2012	0.19	0.10	8.38	0.33	61.98	2.81	0.10	17.54	1.27	2.92	0.10	4.29
	21 Mar 2012 - 18 Apr 2012	0.24	0.12	13.13	0.12	43.77	1.26	0.12	25.54	0.61	10.70	0.12	4.26
ash	2010 (mean composition)	10.09	1.17	19.74	1.45	40.77	1.02	6.86	7.66	3.06	3.02	2.28	2.89

* Suspension of the activities of the steel plant

During the period considered, OCDD accounted for more than 65% of the total mass of PCDD/Fs, giving credit to the possible influence of wood burning (Table 3.4). Furthermore, site 1 is an urban site, thus wood combustion can effectively be an additional source of PCDD/Fs. Two exceptions for the annual variation of the PCDD/F deposition at site 1 were observed: with respect to the adjacent months, a higher deposition (2.49 pg I-TEQ m^{-2} d^{-1}) was measured in summer, during the period 29 June – 8 August 2011, whilst the highest value (3.85 pg I-TEQ m^{-2} d^{-1}) was observed during the period 8 September – 3 October 2011 (Table 3.3). The last sample showed the highest value for the PCB deposition (1.54 pg I-TEQ m^{-2} d^{-1}). During the same period, high peaks of PM concentration were recorded by an air quality monitoring station, managed by the Environmental Protection Agency of the Autonomous Province of Trento (APPA Trento), located about 100 m far from site 1. Further investigations performed by APPA Trento pointed out that such peaks occurred day-time at regular intervals of 20 minutes, giving the reason to believe that the release of PM could not be attributed to the steel plant (that operated regularly night-time) but to an automatic system, such as an industrial combustor. To evaluate this hypothesis, the PCDD/F congener profiles of the atmospheric deposition measured at site 1 were compared to the chemical fingerprint of several known sources (*e.g.*, waste incineration, crematoria, sewage sludge incineration, tire combustion, diesel vehicles, industrial wood combustion, industrial oil boilers and coal combustion) reported in a previous study (US EPA, 2006). The PCDD/F congener profiles well mirrored the congener distribution due to the typical emissions from industrial wood combustion (Figure 3.3), leading to conclude that a malfunctioning combustor fed with industrial wood could be a possible explanation for this episode. The combustion of treated wood, compared with raw wood, is responsible for higher PM emissions due to the presence of chemicals and inert impurities (Tatàno

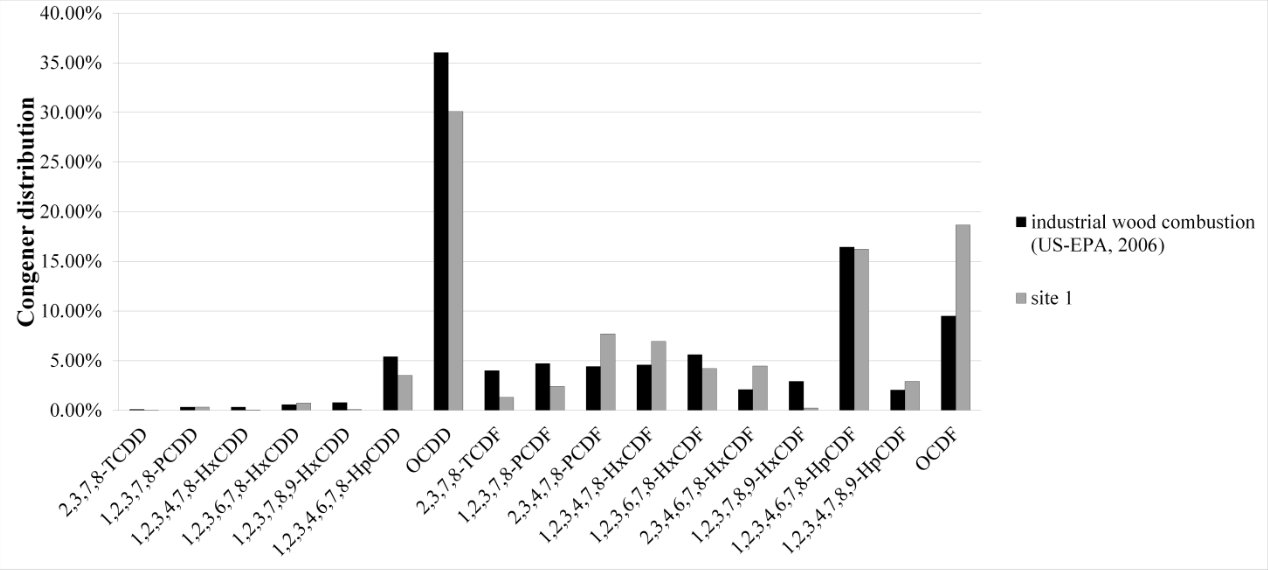

Figure 3.3: Comparison between the PCDD/F congener distribution observed at site 1 during the period 8 September – 3 October 2011 and the distribution reported in a previous study on industrial wood combustion (US EPA, 2006).

et al., 2009). Incomplete combustion of treated wood can contribute to the formation of chlorinated compounds in particulate phase that are subsequently subject to atmospheric deposition to soil.

By a comparison between the congener distribution at site 3 during the peak episode of 12 January – 22 February and the results of previous studies, the domestic combustion of waste resulted as the most plausible reason for this episode: indeed, the prevalence of some congeners (1,2,3,4,6,7,8-HpCDD, OCDD, 1,2,3,4,6,7,8-HpCDF and OCDF) is typical of this process (US EPA, 2006; Solorzano-Ochoa et al., 2012).

Given the representativeness offered by PCBs as markers of the emissions from this sector, in view of the application of dispersion models to simulate the impact of this kind of plants and decide the positioning of deposimeters, PCBs should be adopted as the most appropriate family of compounds for the calibration of models. Since several dispersion models (*e.g.*, AERMOD, CALPUFF, CALGRID, AUSTAL2000) support the calculation of dry and wet depositions, PCB deposition measurements can be used to calibrate PCB emissions whereas analyses on the gas and particle flow composition are not available (*i.e.*, diffuse emissions). The calibration of the emissions is feasible and reasonable when there is certainty that the emission source is the dominant PCB source.

3.3.4 Conclusions

Deposimeters are useful devices to monitor the local impact of POP emissions and detect the dominant emission sources. The implementation of networks of deposimeters could provide indirect information on the level of contamination of agricultural fields and pastures, although a routine monitoring of the PCDD/Fs and PCBs deposition fluxes is still not prescribed by the current environmental legislation. Coupling deposition monitoring with interpretation of the congener profiles can give indications on the presence of activities (normally unmonitored) leading to critical contributions of POPs to atmosphere and soil. By comparing the PCDD/F congener profiles measured at the three sampling sites with the typical congener distribution of the emissions from electric arc furnaces, the influence of the steel plant seemed to be poor and less significant than other PCDD/F sources, like domestic combustion and uncontrolled waste burning, which can represent a threat to plots assigned to agricultural and zootechnical use.

3.4 Assessment of the influence of local sources of POPs through analyses on sediments

Based on: Argiriadis, E., Rada, E.C., Vecchiato, M., Zambon, S., Ionescu, G., Schiavon, M., Ragazzi, M., Gambaro, A., 2013. Assessing the influence of local sources on POPs in atmospheric depositions and sediments near Trento (Italy). *Atmospheric Environment* 98, 32-40. The final publication is available at Elsevier via http://dx.doi.org/10.1016/j.atmosenv.2014.08.035.

3.4.1 Introduction

In-place burial, re-suspension or erosion appear to be the predominant fates of POPs adsorbed on soil particles (Kulkarni et al., 2008). These micropollutants can easily reach aquatic sediments due their ubiquitous character and their resistance to chemical and microbiological degradation (Tamamura et al., 2009). Through atmospheric deposition, POPs are directly conveyed from the source to residential and background areas. PAH sources are mainly represented by industrial and vehicle emissions and wood and fuel combustion (Gambaro et al., 2009; Ravindra et al., 2008). PAHs can also be formed due to heating by electric arc and the use of carbon as an additive (Baraniecka et al., 2010; Yang et al., 1998). PCBs have ubiquitous distribution in the environment, where they are regarded as tracers of anthropic global contamination. PCBs were produced in great amounts up to the 1990s as additives for dielectric fluids, lubricants, and many other applications (Erikson, 1997; Breivik et al., 2004, 2002). As highlighted in Sections 3.2 and 3.3, PCBs are also produced by the metal industry.

An additional monitoring campaign on the influence of the steel plant presented at Section 3.1 was carried out between 2011 and 2012 and the collected data were elaborated in 2014, during this doctoral research. This monitoring campaign focused on the above-mentioned classes of POPs in the sediments of a pond located in the area surrounding the steel plant (site 2 in Figure 3.4). The concentrations of PCBs and PAHs in the sediments were measured. The congener profiles of PCBs and the diagnostic ratios of PAHs were calculated in order to derive indications on the dominant sources in the area of study. Site 1 coincides with the primary school where deposition samples were taken during a parallel activity (Section 3.3).

3.4.2 Material and methods

The area is delimited by two urban settlements on the eastern and western sides, of about 6900 and 2800 inhabitants, respectively. The artificial pond was created in 1996 and is located at about 1 km west of the steel plant, in a biotope established in 1992, where several streams keep the stagnation of water constant. The area is bordered on the south by an important state highway (red in Figure 3.4), crossed in this stretch by more

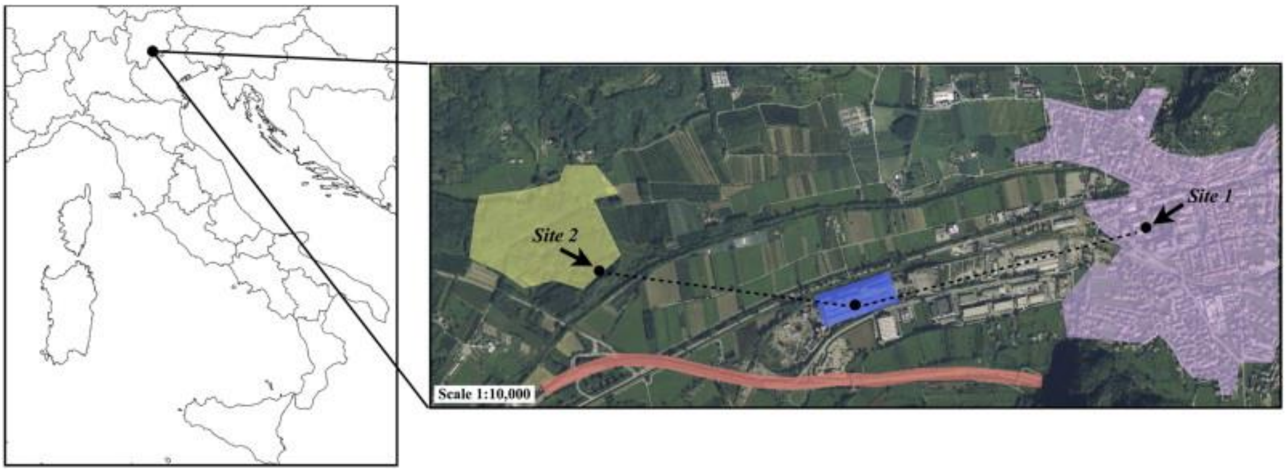

Figure 3.4: Position of the steel plant (blue), the state highway (red) and sampling sites where depositions (site 1) and sediments (site 2) were collected.

than 20,000 vehicles per day.

A manual core drilling was performed on 8 March 2012 down to 24 cm depth. The core was then divided into 8 sections of about 3 cm each. The sediments were dried at ambient temperature up to constant weight and sieved (2 mm). Aliquots from dried sediments were sieved at 63 μm in order to determine coarse (sand) and fine (silt and clay) fractions by means of a sieve shaker (CISA RP200N, Barcelona, Spain).

For each sub-sample, about 10 g (±0.01) were mixed with Na_2SO_4 to remove humidity, copper for the de-sulphuration (Carlo Erba Reagenti S.p.A., MI, Italy), diatomaceous earth and Ottawa sand (Applied Separations Inc., Allentown, PA, USA) and extracted using a Pressurized Liquid Extraction system (FMS, Inc., Watertown, MA, USA) equipped with stainless steel extraction cells (10 mL). Extraction was performed with a mixture of *n*-hexane:dichloromethane (1:1 v/v) through three cycles at 100 °C and 1500 psi. Before processing each sample, the system was cleaned twice with toluene and twice with *n*-hexane:dichloromethane at 100 °C and 2000 psi. Before extraction, a known amount of 2113C-labelled PCBs and 3 13C-labelled PAHs was added to all samples as the internal standard. All extracts were concentrated to 500 μL under a gentle nitrogen flow at 23 °C (Turbovap II®, Caliper Life Science, Hopkinton, MA, USA). Purification was conducted with an automated system (PowerPrep™, FMS, Fluid Management System Inc., Watertown, MA, USA): samples were loaded onto a packed neutral silica disposable column (previously conditioned with 50 mL of *n*-hexane) and eluted with 30 mL of *n*-hexane (10 mL min^{-1}) followed by 30 mL of an *n*-hexane:dichloromethane mixture (1:1, 10 mL min^{-1}). After every purification cycle, the system underwent three cleaning cycles. The final volume was reduced to 500 μL. 100 μL of isooctane were added and the volume was reduced again to 100 μL. Finally, known amounts of recovery standards were added (13C-PCB-47, 13C-PCB-141 and 13C-Chrysene).

15 priority PAHs and 126 PCBs (including indicators and dioxin-like congeners) were analysed. The determination of PAHs was performed with HRGC (7890, Agilent Technologies, Avondale, USA) coupled with a quadrupole mass spectrometer (MS) (Agilent Technologies 5975C) operating in electron impact mode (EI, 70 eV). The determination of PCBs was carried out with HRGC (Hewlett Packard-Agilent 6890 Series GC System) coupled with HRMS (MAT 95XP, ThermoFinnigan) in electron impact mode (EI, 45 eV). Acquisition was performed using selected ion monitoring. Gas-chromatographic separation was executed on a 60-m HP-5MS column (0.25 mm I.D., 0.25 μm; Agilent Technologies). The GC operating conditions are described in detail elsewhere (Piazza et al., 2013). The quantification was performed through the use of internal standards and the isotopic dilution technique. The results were corrected using the instrumental response factor. Three procedural blanks were prepared and analysed during the sample processing. To check repeatability, the analysis of sample 3 (6-9 cm) was repeated three times: the relative standard deviation was 3-17% for PAHs and 7-26% for PCBs. The results were blank-corrected and the limit of quantification (LOQ) was calculated from the mean blank value plus three times the standard deviation. Where no detectable peak was found in the blank, half of the instrumental limit of detection (LOD) value was used in the calculation of the LOQ. LODs for each single congener are reported elsewhere (Piazza et al., 2013).

3.4.3 Results and discussion

Figure 3.5 and Table 3.8 summarize the concentrations of PAHs measured in the 8 sediment samples. In the upper half of the core, the values are about one order of magnitude higher than in the lower part. Anyway, a peak in concentration for all congeners was measured at 9-12 cm, progressively decreasing towards the surface. The major compounds are the medium-weight ones (fluoranthene, pyrene, benzo[*a*]anthracene, chrysene), which represent on average 70% of the total, while benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and

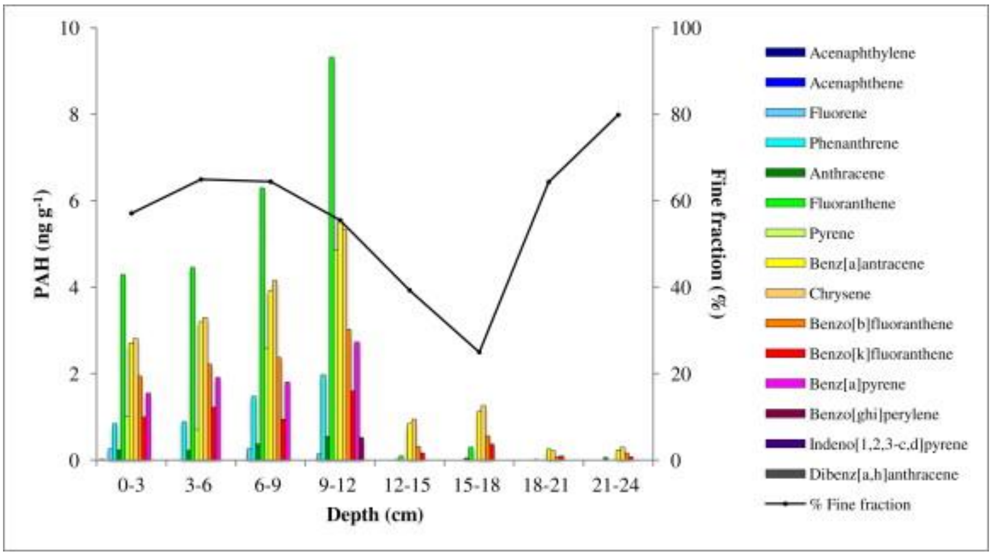

Figure 3.5: PAH concentration (ng g^{-1}) and fine fraction percentage (< 63 µm) in sediment samples.

Table 3.8: Minimum, maximum and average concentrations of PAHs in sediments (ng g^{-1}).

PAH (ng g^{-1})	Min	Max	Mean
Acenaphthylene	n.d.	0.02	0.005
Acenaphthene	n.d.	n.d.	-
Fluorene	n.d.	0.3	0.08
Phenanthrene	n.d.	2	0.6
Anthracene	0.02	0.5	0.2
Fluoranthene	n.d.	9	3
Pyrene	n.d.	5	1
Benz[*a*]antracene	0.2	6	2
Chrysene	0.2	5	2
Benzo[*b*]fluoranthene	0.08	3	1
Benzo[*k*]fluoranthene	0.08	2	0.7
Benz[*a*]pyrene	n.d.	3	1
Benzo[*ghi*]perylene	n.d.	0.5	0.07
Indeno[1,2,3-*c*,*d*]pyrene	n.d.	n.d.	-
Dibenz[*a*,*h*]anthracene	n.d.	n.d.	-

n.d.: not detected

benzo[*a*]pyrene together are the 25%. Fluoranthene is the most abundant congener, ranging from < LOQ in deeper sediments to 9 ng g^{-1} (9-12 cm). With the exception of benzo[*a*]pyrene, 5-ring PAHs were not detected in any sample. The distribution pattern is preserved along the core, as shown in Figure 3.5.

Diagnostic ratios between different congeners (Table 3.9) indicate combustion as the main source (Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012). The dominant congeners are source markers of coal combustion, motor vehicles and incineration (Ravindra et al., 2008).

Concentrations of PCBs are shown in Figure 3.6 and Table 3.10. The distribution is centred on hexa- and hepta-CBs, which on average represent the 72% of the total in the first 6 samples. Here the pattern of homologues is quite constant in the 3-12 cm section, while hepta-CBs almost disappear in the surficial layer (6 pg g^{-1}). With respect to PAHs, the peak in PCBs is visible at a different depth. This may be due to a difference in sources and processes that generate different POPs. PAHs are mainly combustion-derived, while other species are almost exclusively of industrial origin, and this can result in the observed time-shift in sediments. The most abundant species is the indicator PCB-153, ranging from < LOQ to 73 pg g^{-1}. POPs are usually associated with finer particles. Here, both PAHs (Figure 3.5) and PCBs (Figure 3.6) partly follow the trend of the fine fraction of samples (< 63 μm), but other factors may determine the observed distribution. The upper 12 cm may better represent depositional processes, while bottom sediments may date back to the artificial creation of the pond and therefore be less significant to the purposes of this study. The progressive decrease

Table 3.9: Diagnostic ratios for PAHs (ANT: anthracene, PHE: phenantrene, FLA: fluoranthene, PYR: pyrene, BaA: benzo[*a*]anthracene, CHR: chrysene, BaP: benzo[*a*]pyrene, BeP: , IcdP: Indeno(1,2,3-*c*,*d*)pyrene, BghiP: benzo(*ghi*)perylene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene).

Diagnostic ratio	Value	Type of emission
ΣLMW/ΣHMW	< 1	Pyrogenic
	> 1	Petrogenic
ΣCOMB/ΣPAHs	~1	Combustion
ANT/(ANT + PHE)	< 0.1	Petrogenic
	> 0.1	Pyrogenic
FLA/(FLA + PYR)	< 0.4	Petrogenic
	0.4–0.5	Fossil fuel combustion
	> 0.5	Grass, wood, coal combustion
BaA/(BaA + CHR)	0.2–0.35	Coal combustion
	> 0.35	Vehicular emissions
	< 0.2	Petrogenic
	> 0.35	Combustion
PYR/BaP	~10	Diesel combustion
	~1	Gasoline combustion
FLA/PYR	~0.6	Vehicular emissions
IcdP/(IcdP + BghiP)	< 0.2	Petrogenic
	0.2–0.5	Petroleum combustion
	> 0.5	Grass, wood and coal combustion
BbF/BkF	2.5–2.9	Aluminium smelter emissions
BaP/BghiP	< 0.6	Non-traffic emissions
	> 0.6	Traffic emissions

with:

ΣLMW	2+3 rings PAHs
ΣHMW	4+5 rings PAHs
ΣCOMB	FLA, PYR, BaA, CHR, BkF, BbF, BaP, IcdP and BghiP

in concentrations observed in the upper part of the core may be related both to the adoption of BATs by the steel plant and to the adaptation of vehicles to more restrictive environmental regulations.

3.4.4 Conclusions

Patterns and profiles do not allow for the univocal identification of one main source of POPs, while the diagnostic ratios indicate domestic heating and vehicular traffic as important inputs of PAHs to the atmosphere. The analysis of sediments revealed a negative trend of concentrations in time, likely ascribable to the update of regulatory limits of emission and use of POPs, and to the new technologies adopted by the industrial sector. These results highlight the complexity and importance of the constant monitoring of POPs, which allows for the identification of dominant sources and responsibilities. This study is intended as an explorative investigation on levels and processes: further effort is needed to improve the amount of information obtained, for instance by dating sediments and collecting a greater number of samples.

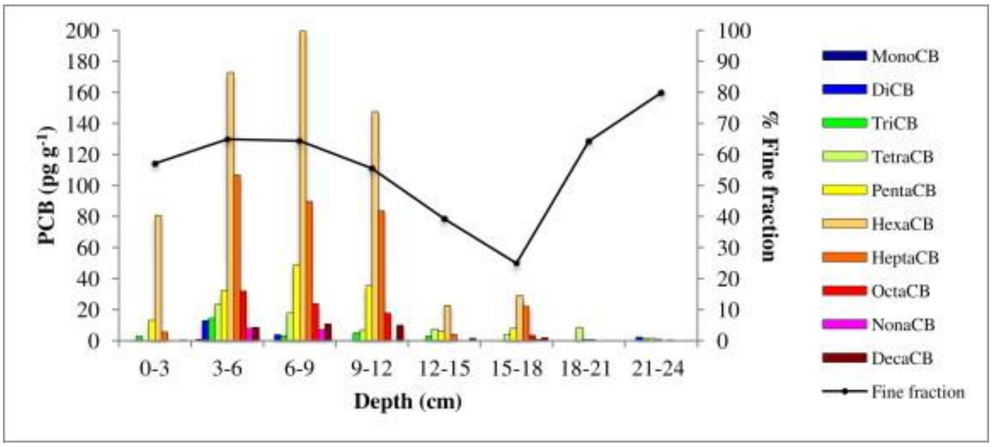

Figure 3.6: PCB concentration (pg g^{-1}) and fine fraction percentage (< 63 µm) in sediment samples.

Table 3.10: Minimum, maximum and average concentrations of PCBs in sediments (pg g^{-1}).

PCB (pg g^{-1})	Min	Max	Mean
Mono-CB	n.d.	0.8	0.1
Di-CB	n.d.	13	3
Tri-CB	n.d.	48	10
Tetra-CB	0.2	23	9
Penta-CB	0.6	49	18
Hexa-CB	0.08	200	82
Hepta-CB	n.d.	107	39
Octa-CB	n.d.	32	10
Nona-CB	n.d.	8	2
Deca-CB	n.d.	11	4

3.5 Assessing the impact of NO_x and benzene emissions on air quality and cancer risk in an urban area

Based on: Schiavon, M., Redivo, M., Antonacci, G., Rada, E.C., Ragazzi, M., Giovannini, L., Zardi, D., 2015. Assessing the air quality impact of nitrogen oxides and benzene from road traffic and domestic heating and the associated cancer risk in an urban area of Verona (Italy). *Atmospheric Environment* 120, 234-243. The final publication is available at Elsevier via http://dx.doi.org/10.1016/j.atmosenv.2015.08.054.

3.5.1 Introduction

In urban areas, the exposure of the resident population to air pollutants is usually higher than in rural contexts. This depends on a combination of intense traffic and other sources of air pollution, contributing to the emission of a variety of substances, including both primary and secondary pollutants. Among primary pollutants, VOCs stand out for the toxicological effects that they may induce, as a consequence of long-term exposure via inhalation. Benzene is considered the most hazardous component among the traffic-related pollutants (Angelini et al., 2012). At a European and North-American level, the transportation sector contributes for more than 80% to the total benzene emissions (Agency for Toxic Substances and Disease Registry, 2007; European Environment Agency, 2007).

Typical secondary pollutants are tropospheric O_3 and NO_2. The latter is naturally produced by oxidation of nitrogen monoxide (NO). NO_2 is also a precursor of O_3, which is linked to the former by a complex mechanism of chemical reactions. Mobile sources contribute for 40.5% to NO_x emissions in Europe, followed by energy production (22.5%), commercial, institutional and household activities (12.8%), energy use in industry (12.6%) and other sectors of minor relevance (11.6%) (European Environment Agency, 2014). Heating systems based on the combustion of natural gas (NG) are widespread in Europe for production of hot water, either for sanitary purposes or as heating source for dwellings, public buildings and commercial activities. Using NG instead of other fossil fuels entails lower emissions of carbon dioxide (CO_2) and substantial absence of other pollutants, with the exception of NO_x, the second most important compounds emitted. Unlike NO (which is a harmless gas at ambient concentrations), NO_2 is known to have detrimental effects on humans, especially on children and people already suffering from lung diseases (Kulkarni and Grigg, 2015), although NO_2 is not a carcinogenic compound.

The compliance with air quality limits is a challenging issue for European urban areas, which are generally characterized by intense traffic, as well as additional sources (*e.g.*, domestic heating, industrial or manufacturing activities), complex urban patterns and, consequently, peculiar micrometeorological situations. In particular, wind intensity, air temperature and humidity are modified in an urban environment, compared to rural areas (Landsberg, 1981; Giovannini et al., 2011, 2013, 2014). On large urban scale, the urban environment induces effects also on rainfall intensity, air quality, formation of fog and hence on livability of urban areas. In addition, the weak ventilation, caused by the presence of buildings, tends to reduce the dispersion of pollutants and increases their concentration, especially during thermal inversions.

The population exposure to air pollutants is then amplified in urban contexts by the lack of open spaces and by the complexity of the urban pattern, including relatively narrow channelled streets, lengthwise delimited by buildings. Stretches of roads displaying these features are identified as street canyons. If the ratio between the average height of the buildings and the width of the canyon is high enough to establish skimming flow conditions (at least higher than 0.65), the retention of pollutants within the urban canopy layer is amplified (Oke, 1988; Chan et al., 2003). Indeed, the main feature of a street canyon is to further favour the establishment of a strongly local air circulation, consisting in a helical vortex with an axis parallel to the canyon direction. Under these conditions, the transport of pollutants out of the canyon is limited.

As highlighted in Section 2.3.2.8, the punctual measurements performed by the conventional air quality monitoring stations are generally not representative of large areas, due to the complex morphology of the urban environment. For this reason strategic policies for air quality mitigation can be conveniently pre-evaluated by emission and dispersion models, which allow improving the spatial representativeness of the punctual measurements, thus extending the information on ambient air concentrations to a wider area. Several studies, combining air quality monitoring with a modelling approach, focused on the role of urban street canyons in determining critical situations of air pollution (Murena, 2007; Vardoulakis et al., 2005; Borge et al., 2014; Eeftens et al., 2013; Gallagher et al., 2013; Dons et al., 2014; Schiavon et al., 2014a). However, the effect of emission sources other than traffic has not been modelled, in spite of the importance of other sectors, and in particular domestic heating, in determining the current air pollution levels.

Given the peculiarity of the urban environment in terms of emission and dispersion of air pollutants, this part of this doctoral research has three main purposes: highlighting the importance of modelling activities as a tool to detect critical levels of exposure that the conventional air quality monitoring networks are not able to identify; investigating the role of the dominant sources of air contaminants in an urban area; studying the interaction of air pollutants with the urban morphology, characterized by the presence of street canyons. In particular, this study focuses on the evaluation of NO_x concentrations and on the comparison between the role of traffic and domestic heating, the two major sectors contributing to NO_x emissions. In addition, the cancer risk related to the exposure to benzene is estimated, considering the contribution of road traffic only, since emissions from vehicles are the dominant source in urban environments. The methodology adopted to reach the aforementioned goals is based on simulations by means of emission and dispersion models, and by the adoption of the US EPA cancer risk approach (US EPA, 2005b).

3.5.2 Material and methods

3.5.2.1 Area of study

The target area for the present investigation is the town of Verona (Italy), a typical mid-sized urban area (nearly 400,000 inhabitants, including suburban surroundings) located in the Po Plain, which is known as one of the most air-polluted areas in Europe, for a combination of high emission levels and unfavourable meteorological conditions. The climate characterising this region is continental and episodes of both ground-based and elevated thermal inversion frequently occur during winter (Rampanelli and Zardi, 2004; Andrighetti et al., 2008). Verona is the crossing of two main corridors, namely the north-south connection between Central Europe and Italy, along the Brenner corridor, and the connection between eastern and western areas of northern Italy. As a consequence, it is daily crossed by intense traffic flows. Also, a strong contribution to air pollution comes from the traffic of daily commuters between the densely inhabited peri-urban area and the inner city.

The modelling activity focused on a neighbourhood of Verona, named Borgo Roma. To monitor the traffic within the urban area of Verona, a monitoring network was activated by the Municipality in 2009. The transits are detected by inductive loops embedded into the road surface. Borgo Roma is characterized by high traffic, high population density (> 20,000 inh km^{-2}) and presence of many different schools (from kindergartens to high schools). Unlike other areas of Verona, Borgo Roma is not served by the centralized district heating system of the town. As a consequence, dwellings are heated up either by household hot-water heaters or by one central heater per building. Both heating systems are fuelled with NG. In the absence of a district heating system, NO_x emissions are locally produced, and add to the contribution from road traffic. Two main roads of Borgo Roma can be classified as urban street canyons, namely Via Scuderlando and Via Centro. The combination of canyon-like roads and high traffic fluxes, associated with potentially high release of benzene from road traffic, high population density, conspicuous number of scholars (thus, sensitive receptors) and additional local sources of NO_x beyond road traffic, makes Borgo Roma a potentially critical area in terms of impact on human health. An air quality monitoring station measuring NO_x is present within the area of study, along one of the major roads of the neighbourhood (Via San Giacomo). This allowed comparing the results of the simulations with data from measurements. Moreover background concentrations were retrieved by a rural air quality monitoring station, 8-km far from Borgo Roma. Finally benzene concentrations, measured by a station located along an urban road of Verona (outside Borgo Roma) characterized by intense traffic, were compared with the results from simulations.

3.5.2.2 Calculation of emissions

Hourly mean fluxes of vehicles typically occurring both in a summer and in a winter week were retrieved. Information on the typical vehicle fleet of Verona was retrieved from the 2012 Italian car census provided by the Automobile Club Italia (ACI). NO_x and benzene emissions were estimated by using the COPERT 4 algorithm. This tool contains a large database of emission factors for a wide number of classes of vehicles and motorcycles. The calculation of the emission factors (expressed in g km^{-1} veh^{-1}) is mostly based on empirical relations, specific for each vehicle class. In particular, these relations depend on the mean vehicle speed and the annual mean air temperature. The emission factors for NO_x, CO and VOCs are increased by an amount which accounts for “cold emissions”, since these compounds are removed by the three-way catalysts, which are ineffective at low temperatures (Ntziachristos and Samaras, 2000). VOC speciation is also available (European Environment Agency, 2013), so that emissions of benzene can be easily calculated. Hourly average emissions of NO_x and benzene (expressed in g s^{-1}) along each stretch of road were calculated on the basis of the hourly vehicle fluxes, the length of the stretch, the composition of the vehicle fleet and the emission factors provided by COPERT 4. A mean driving speed of 40 km h^{-1} and an annual mean temperature of 15 °C were assumed for the calculation.

Simulations considering a scenario without the circulation of pre-EURO 1 and EURO 1 vehicles were also performed, to investigate the effects of environmental policies including restrictions to the circulation of highly polluting vehicles. Indeed, several municipalities in northern Italy have adopted such restrictions to improve air quality. Therefore, in this additional scenario, NO_x and benzene emissions were calculated only for vehicles satisfying at least EURO 2 requirements.

Detailed data on the consumption of NG and on the technologies of heaters of every building in the study area were provided by the municipal company AGSM, which is the main provider of services such as gas and district heating in the town. Beside NG consumption for cooking, which was assumed to be negligible with respect to the total consumption, NG is used both for domestic heating and to produce hot water for sanitary use. However, the use of NG for domestic heating in Verona is restricted to the period 15 October – 15 April, and for a maximum number of 14 hours per day. On the other hand, hot-water heaters operate during the whole year, even though with large differences in the consumption between winter and summer: the ratio between the mean NG consumption in summer and in winter is about 0.1. Furthermore, on the basis of the available data, the mean NG consumption can be sub-divided into three modulations, approximating the monthly, the daily and the hourly consumption normalized to the annual, the monthly and the daily averages, respectively. Finally, in the target area of the present study, buildings can be divided into three main categories: residential buildings, school buildings and commercial activities or offices. Given these considerations, three different sets of modulations can be assumed (Table 3.11).

In order to evaluate the rate of conversion of NG into air pollutants, the working conditions of the most diffused heating plants were taken into account. The NG-fuelled household heaters in use in Italy belong to three main categories: conventional, pre-mixed and condensing boilers. In assigning NO_x emission factors, household heaters were evaluated separately from central heaters (*i.e.*, a single heater serving all the flats of a building). Central heaters can be further divided into three main categories as well, *i.e.*, conventional, condensing and modulating boilers. Condensing boilers are considered an emerging technology, since they recover the latent heat of vaporization of the water produced in the combustion process by condensing the water vapour to liquid. The typical NO_x emission factors for household and central heaters available on the Italian market are listed in Table 3.12, on the basis of the technological solution implemented. The same emission factors were adopted in the calculation of the emissions. The hourly NO_x emissions for each source were calculated by assuming a lower heating value of 35.88 MJ Nm^{-3} for NG. Besides the scenario representing the current situation, an additional scenario was created to simulate the improvements achievable if all the hot-water heaters were condensing boilers.

Table 3.11: Modulations of NG consumption, approximating the monthly, the daily and the hourly consumption normalized to the annual, the monthly and the daily one, respectively.

Type of building	Month											
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Residential	0.188	0.188	0.094	0.075	0.022	0.022	0.022	0.011	0.022	0.075	0.094	0.188
School	0.188	0.188	0.094	0.075	0.033	0.033	0.000	0.000	0.033	0.075	0.094	0.188
Commercial	0.166	0.139	0111	0.083	0.056	0.028	0.028	0.000	0.056	0.083	0.111	0.139

Type of building	Day						
	Mon	Tue	Wed	Thu	Fri	Sat	Sun
Residential	0.033	0.033	0.033	0.033	0.033	0.033	0.033
School	0.042	0.042	0.042	0.042	0.042	0.042	0.000
Commercial	0.051	0.051	0.051	0.051	0.026	0.000	0.000

Type of building	Hour																							
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Residential	0.000	0.000	0.000	0.000	0.000	0.077	0.077	0.077	0.077	0.000	0.000	0.077	0.077	0.000	0.000	0.000	0.077	0.077	0.077	0.077	0.077	0.077	0.077	0.000
School	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.100	0.000	0.000	0.000	0.000	0.000	0.000
Commercial	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.125	0.125	0.125	0.125	0.000	0.000	0.125	0.125	0.125	0.125	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Table 3.12: NO_x emission factors adopted for household heaters and central heaters.

Size	Technology	NO_x emission factor [$g\ GJ^{-1}$]	Reference
Household heaters	Conventional boilers	50	EEA, 2013
	Condensing boilers	15	Bassi et al., 2005
	Pre-mixed boilers	17	Bassi et al., 2005
Central heaters	Conventional boilers	37	Bassi et al., 2005
	Condensing boilers	7	Bassi et al., 2005
	Modulating boilers	42	Bassi et al., 2005

3.5.2.3 Dispersion model

For the simulations of NO_x and benzene dispersion, the model AUSTAL2000 was adopted. AUSTAL2000 is a lagrangian particle model which computes the transport of pollutants in the lower atmosphere at a local scale. AUSTAL2000 is able to take into account both horizontally and vertically variable meteorological and turbulence fields. The vector of turbulent velocity is randomly varied by simulating a Markov process and the random parameters vary with the intensity of turbulence. The concentration is then computed by counting the particles in a given volume. AUSTAL2000 contains a diagnostic (mass-consistent) flow model called TalDIA; this module works on profiles of wind and classes of atmospheric stability to perform an economical calculation of the wind flow fields. TalDIA can take into account both orographic complexity and building effects, through the superposition of an unperturbed uniform flow field with one affected by obstacles (Umwelt Bundesamt, 2009).

Taking advantage of this capability of the model, in this study the geometry of buildings was explicitly defined. Indeed, when zooming to the urban-canyon scale, the problem of considering the urban geometry explicitly is mandatory to adequately resolve local microclimatic conditions and, as a consequence, the heterogeneities in the spatial distribution of pollutants (Burian et al., 2006). In fact, in these complex cases, specific processes occur (Rotach and Zardi, 2007; Giovannini et al., 2011, 2013, 2014) that modify local circulations and turbulence mixing in the atmospheric boundary layer (de Franceschi and Zardi, 2009), making the study of air pollution more complicated (Antonacci and Tubino, 2005; de Franceschi and Zardi, 2009; Gohm et al., 2009; Rada et al., 2011; Ragazzi et al., 2013a).

The computation domain used in this study is a rectangular area of 720 × 1035 m^2, including Via Centro and the most canyon-like part of Via Scuderlando, in addition to other important streets of the area (Figure 3.7). A cell size of 5 m × 5 m was chosen to represent the situation inside street canyons. The map containing the heights of the buildings was generated with the same resolution. Data on wind speed, wind direction and atmospheric stability classes were retrieved from a meteorological station managed by the local Environmental Agency (ARPAV) and located near the area of study. The meteorological data refer to the whole year 2012, to be consistent with the data on the vehicle fleet. The reference meteorological station, actually located outside of the domain, was fictitiously re-located inside the computation area, north to the buildings, since the model requires the position of the anemometer inside the domain. Since the terrain around the buildings

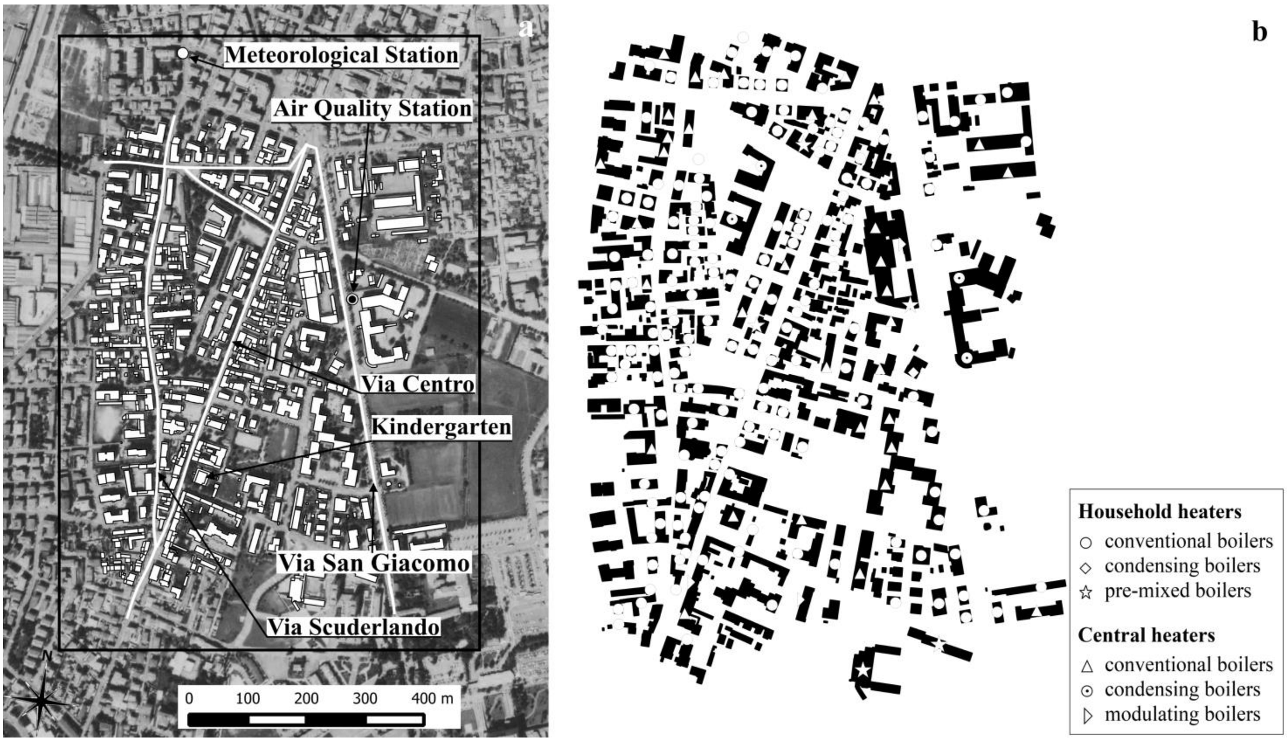

Figure 3.7: *a)* Area of study with representation of the computation domain and *b)* detail of the emission points representing the hot-water heaters.

included in the calculation is flat, this shift from the real position to a fictitious location does not influence the calculation of the wind field inside the area covered by the building map.

Emissions from traffic were assimilated to line sources following the development of the streets, whilst domestic hot-water heaters were represented by point sources. With regards to roads, the height of the emission source was set to 0.5 m above the ground and a vertical extension of the source (varying between 1.0 m for street canyons and 0.5 m for the remaining roads) was set to simulate the mechanical turbulence production by vehicle motions, which influences the pollutant dispersion at the source level.

With regards to hot-water heaters, the source height was set as equal to the height of the top of the chimneys, that is 0.5 m above the roof, in compliance with the Italian technical regulation UNI-CIG 7129 (UNI, 2008). In the absence of mechanically produced turbulence, the vertical extension of the source was set at 0.05 m, corresponding to the lateral opening of the chimneys. The emission points representing the chimneys of the buildings and the details of the hot-water heaters, classified by technology and size (household or central heaters) are reported in Figure 3.7b. Outside the area covered by buildings, the surface roughness was set to 0.9 m: as Borgo Roma is characterized by a very heterogeneous land use, this is an average roughness length between the value suggested in the CORINE maps for continuous coverage of buildings (1.0 m) and for areas with commercial and manufacturing activities (0.8 m) (Silva et al., 2007).

3.5.2.4 Cancer risk estimation

Since benzene is a carcinogenic pollutant, the estimation of the inhalation cancer risk related to the exposure to benzene was performed. The calculation is based on the concept of UR_{inhal}, defined by the US EPA as the upper-bound excess lifetime cancer risk deriving from continuous exposure to 1 μg m^{-3} of a carcinogenic compound in air (US EPA, 2015a). The UR_{inhal} adopted for benzene is 2.9E-05 (California Environmental Protection Agency, 2009), a more precautionary value with respect to its last formulation by the US EPA (US EPA, 2015b); the value here adopted considers possible differential effects on the health of infants (California Environmental Protection Agency, 2009). Thus, the annual mean concentrations of benzene were multiplied by the UR_{inhal}.

3.5.3 Results and discussion

3.5.3.1 NO_x concentrations

The maps of the annual mean concentrations of NO_x induced only by road traffic are presented in Figure 3.8. If considering the whole vehicle fleet, the highest value of NO_x concentrations is 61.9 μg m^{-3} and occurs near the junction between the two street canyons (Figure 3.8a). This may be explained by considering that these joining canyons are one-way streets and, in the proximity of their junction, the circulation becomes

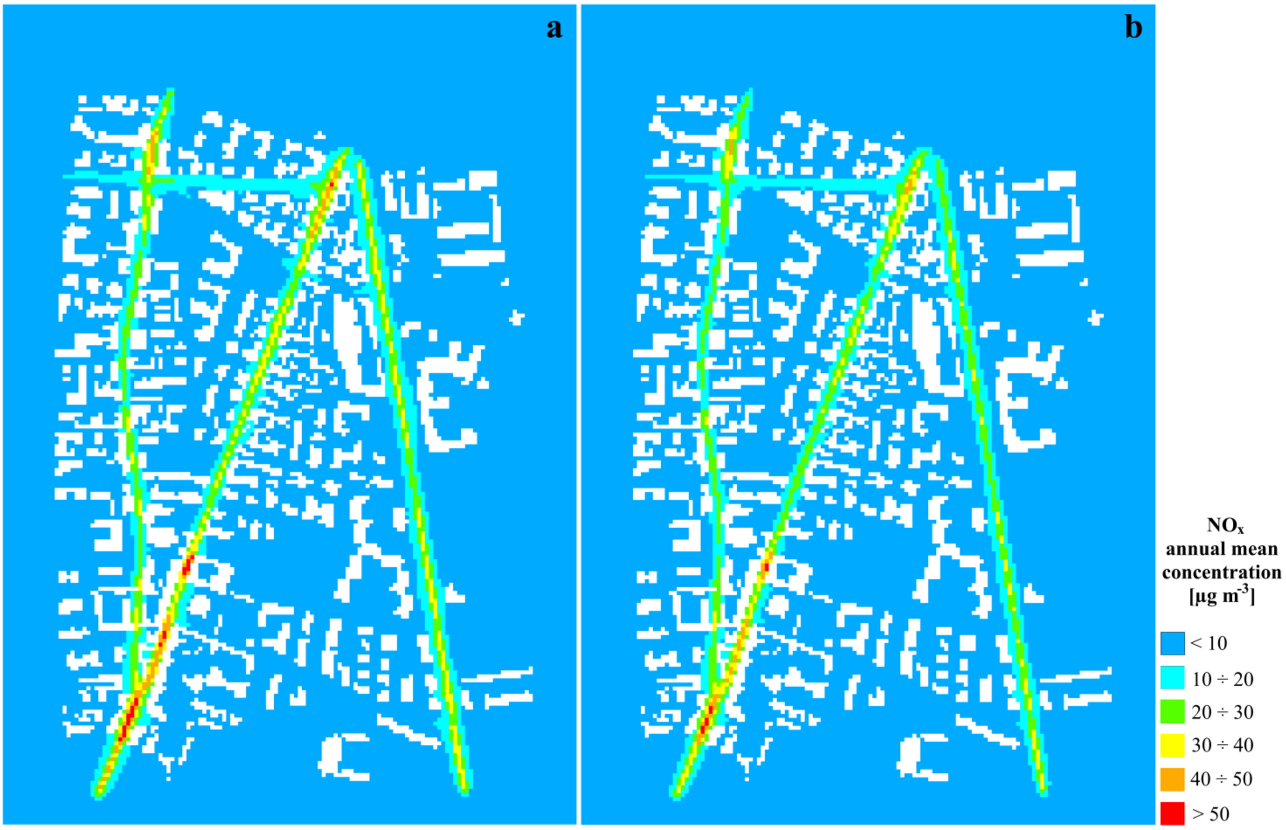

Figure 3.8: Maps of the NO_x annual mean concentrations induced *a)* by the whole vehicle fleet and *b)* only by the EURO 2 and latest vehicles.

two-way. It is significant to note that slightly lower NO_x levels also occur inside Via Centro with a maximum of 58.5 µg m^{-3}. Indeed, next to this point the canyon width is minimum (10 m), and the buildings display an average height of 10.5 m. It is important to notice that a kindergarten is located near this point. Thus, this concentration level is of great relevance from the toxicological point of view. Lower concentrations occur within Via Scuderlando, although a value of 48.2 µg m^{-3} is observed in the northern stretch of the canyon. The current situation improves in the scenario forbidding the most polluting vehicles (pre-EURO 1 and EURO 1) to circulate (Figure 3.8b). On average, the NO_x mean annual concentrations are about 13% lower than with the whole vehicle fleet. Like in the previous case, the highest value occurs at the junction between the two canyons (54.6 µg m^{-3}). A concentration of 51.6 µg m^{-3} is achieved in the proximity of the kindergarten of Via Centro.

Inside street canyons, the NO_x annual mean concentrations induced by hot-water heaters represent about 25% of the NO_x annual mean concentrations induced by road traffic (Figure 3.9a). The contribution of domestic heating is generally higher far from roads, where the impact of the emissions from road traffic is less important. However, the highest NO_x annual mean concentration (14.4 µg m^{-3}) occurs in the proximity of a building close to Via Scuderlando. Concentrations up to 13.7 µg m^{-3} occur in a courtyard of a building near Via San Giacomo. As the chimneys are located close to the limit of the urban canopy layer, and not inside the street canyons, their contribution also affects background areas. Since the concentration maps are calcu-

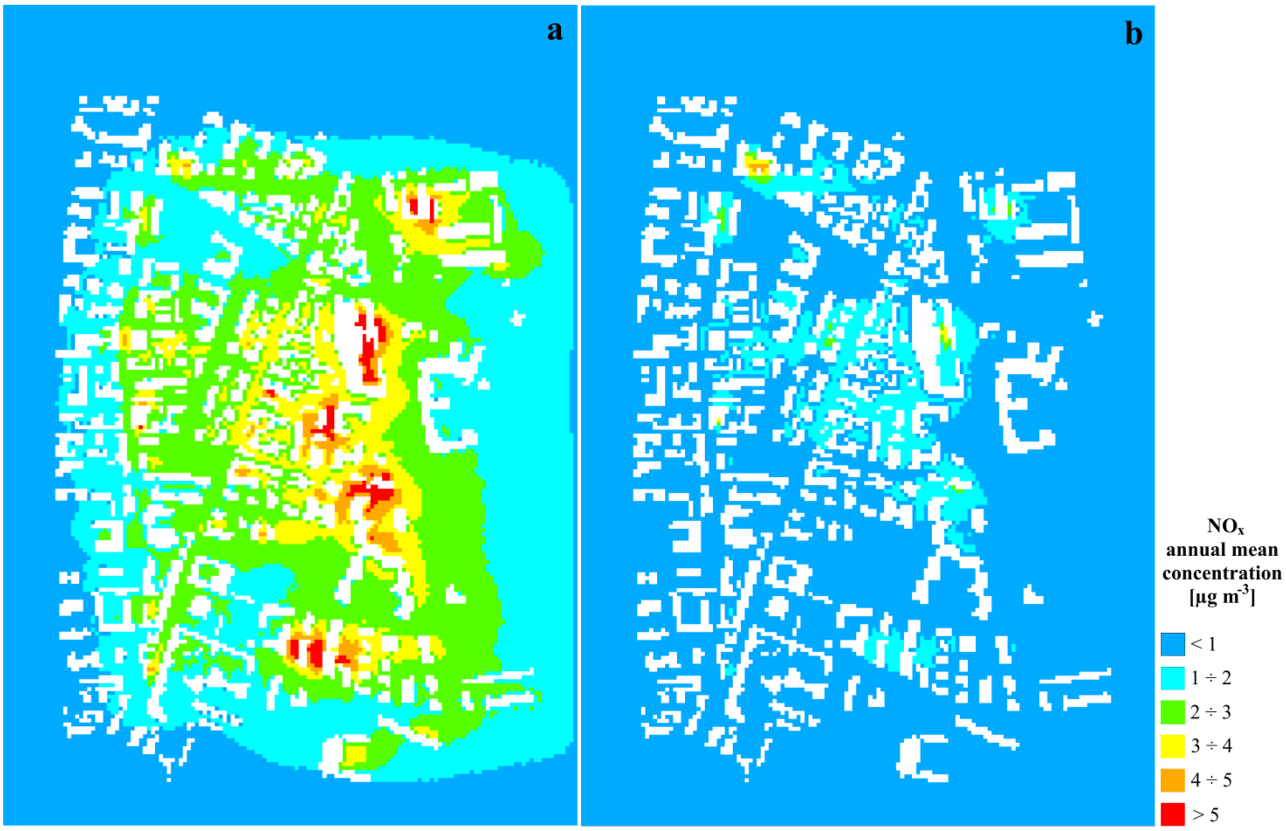

Figure 3.9: Maps of the NO_x annual mean concentrations induced *a)* by the current hot-water heaters and *b)* in the hypothesis of replacing the current hot-water heaters with condensing boilers.

lated on an annual basis, the contribution from domestic heating is expected to be much more influent during winter. Appreciable improvements could be obtained by adopting more efficient (and less polluting) hot-water heaters, such as condensing boilers (Figure 3.9b). In this case, the highest NO_x annual mean concentration reduces to 4.9 µg m^{-3}, which is achieved in a courtyard surrounded by buildings, in the proximity of Via Scuderlando.

The NO_x annual mean concentrations induced by road traffic and domestic heating were finally added up to the NO_x annual mean concentration measured by the rural air quality station (54.4 µg m^{-3}). The highest NO_x annual mean concentration (117.8 µg m^{-3}) still occurs at the junction between the two street canyons (Figure 3.10a). Concentrations up to 115.3 µg m^{-3} occur at the bottleneck of Via Centro, about 50 m from the kindergarten. Important improvements could be achieved by introducing restrictions to the circulation of the most polluting vehicles (pre-EURO 1 and EURO 1) and, at the same time, adopting more efficient (and less polluting) hot-water heaters, such as condensing boilers (Figure 3.10b). In this case, the highest total NO_x mean concentration, on an annual basis, is 109.4 µg m^{-3}, still located at the junction between the two street canyons. Inside street canyons, a 10% reduction of NO_x annual mean concentrations is estimated.

The model results were validated by comparing the NO_x hourly measurements taken at the urban air quality station of via San Giacomo with the total NO_x hourly concentrations obtained by summing the results of

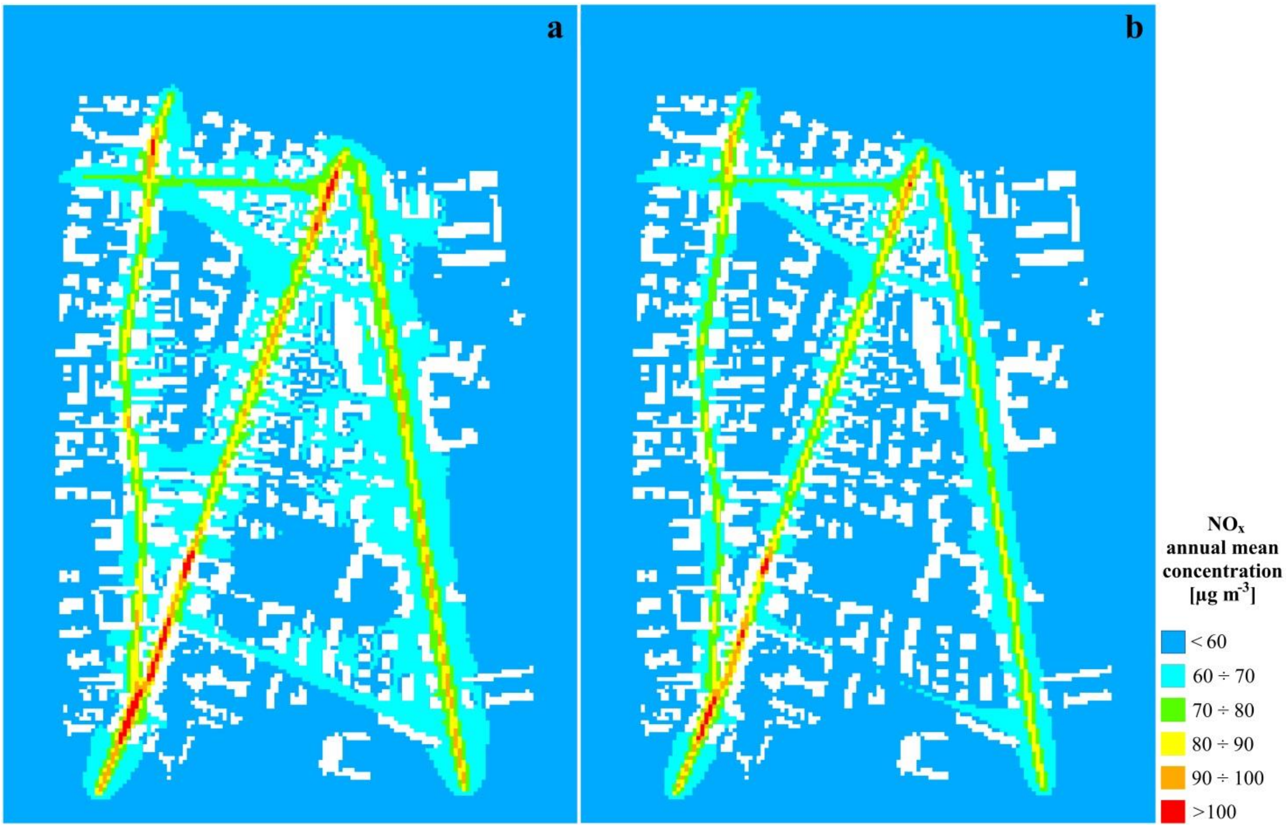

Figure 3.10: Maps of the NO_x annual mean concentrations induced by *a)* the whole vehicle fleet together with the current hot-water heaters in use and *b)* in the hypothesis of allowing the circulation only to EURO 2 and newer vehicles and replacing the current hot-water heaters with condensing boilers.

model (at the receptor point corresponding to the urban air quality station) with the hourly concentrations measured by the rural air quality station. The annual mean concentration calculated by the model is 69.8 µg m^{-3}; the 25th, 50th, 75th and 95th percentiles of the hourly concentrations are 30.8, 51.7, 83.9 and 193.1 µg m^{-3}, respectively. The annual mean concentration measured at the same location by the urban air quality station during 2012 is 111.0 µg m^{-3} and the 25th, 50th, 75th and 95th percentiles are 32.0, 62.0, 148.0 and 363.0 µg m^{-3}, respectively.

The lowest percentiles (25th and 50th), calculated by the model, are in good agreement with those measured, but the highest percentiles (75th and 95th) are considerably lower with respect to the corresponding statistics calculated from the measurements. This may be due to emission peaks (*e.g.*, traffic congestions or simply higher traffic fluxes) occurred during periods of the year not covered by the traffic data used in this study. Such situations could be adequately considered by coupling the meteorological data with hourly traffic data covering the whole solar year. However, it is worth reminding that other sources (*e.g.*, energy production and distribution, industrial activities, agriculture, non-road transport) may contribute to NO_x concentrations, but their role was not included in this study due to the difficulties in localizing all the sources, retrieving their emission factors and modelling the respective emissions.

3.5.3.2 Benzene concentrations

The annual mean benzene concentrations induced from the whole vehicle fleet exceed the limit value (5 µg m^{-3}) at the junction between the two street canyons (maximal value of 6.7 µg m^{-3}), in the southern end of Via Centro (maximal value of 5.7 µg m^{-3}), at the bottleneck of Via Centro (6.4 µg m^{-3}), at the northern end of the same street (5.8 µg m^{-3}) and in the canyon-like part of Via Scuderlando (5.3 µg m^{-3}) (Figure 3.11a). Forbidding the circulation to pre-EURO 1 and EURO 1 vehicles results in the compliance with the limit value in the whole domain (Figure 3.11b).

Benzene concentrations induced by EURO 2 and newer vehicles in the street canyons are about 43% lower than the concentrations induced by the whole vehicle fleet. The effect of the more and more restrictive limits on hydrocarbons, imposed by these emission standards, is clearly visible. The annual mean concentration measured during 2012 by the urban air quality station taken as reference for benzene was 1.81 µg m^{-3}. This value is similar to the annual mean concentration calculated in the proximity of the kindergarten and considering the whole vehicle fleet (1.65 µg m^{-3}). The 25th, 50th, 75th and 95th percentiles of the series measured are 0.8, 1.5, 2.7 and 4.4 µg m^{-3}, respectively, and the maximum value is 5.9 µg m^{-3}. These values are also comparable with the concentrations calculated by AUSTAL2000 in the vicinity of the kindergarten (25th percentile: 1.1 µg m^{-3}; 50th percentile: 1.6 µg m^{-3}; 75th percentile: 2.1 µg m^{-3}; 95th percentile: 2.7 µg m^{-3}; maximum: 3.4 µg m^{-3}). Slightly lower concentrations were calculated in the vicinity of the air quality station of Via San Giacomo. Due to the absence of rural stations measuring benzene, no background concentrations were considered.

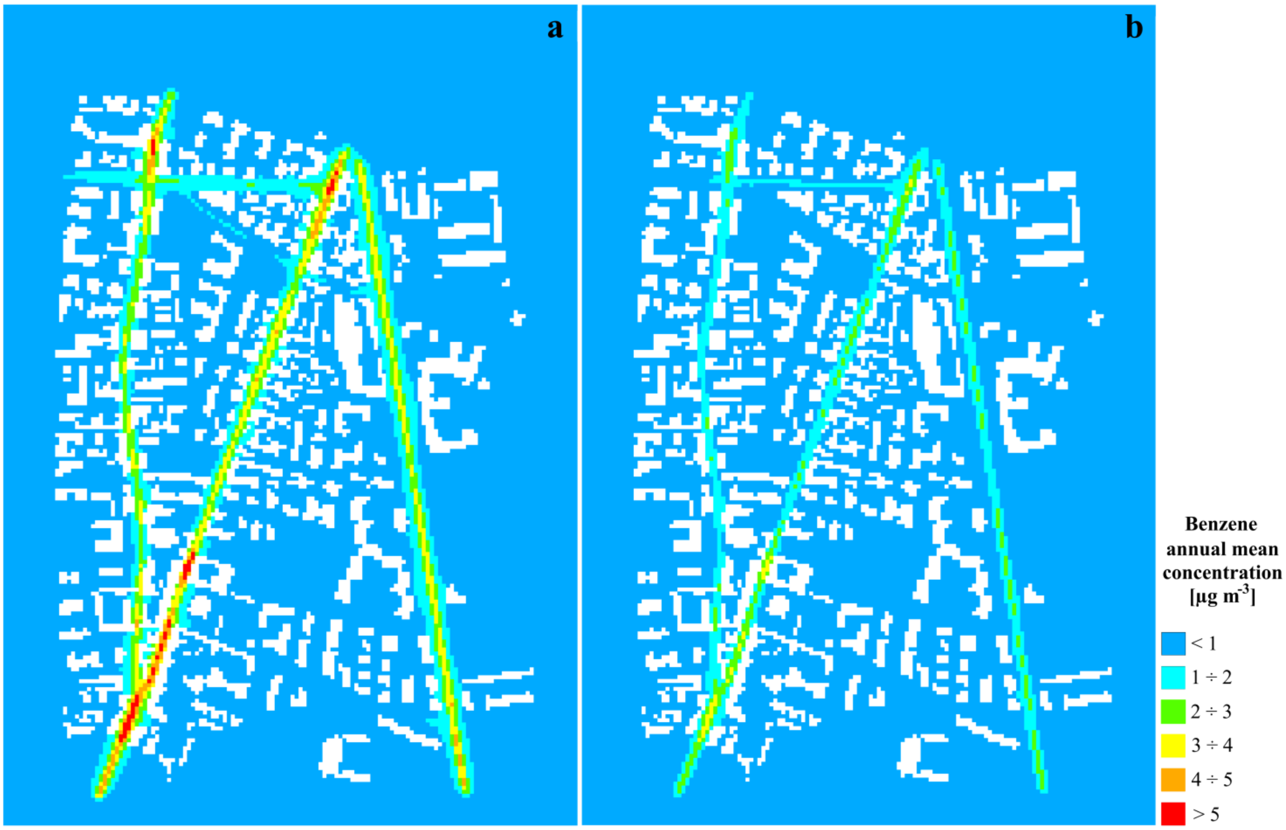

Figure 3.11: Maps of the benzene annual mean concentrations induced *a)* by the whole vehicle fleet and *b)* only by the EURO 2 and latest vehicles.

The related maps of the cancer risk induced by continuous and long-term exposure to benzene are presented in Figure 3.12a, when considering the whole vehicle fleet. It is important to remind that such maps report only the benzene-related cancer risk induced by road traffic. In the area of study, contributions from other sectors are secondary, since other potential sources of benzene like industrial activities are not located inside the domain.

Since the inhalation cancer risk is proportional to the concentration, the highest value (1.95E-04) occurs at the junction between the two street canyons, while a slightly lower risk value (1.85E-04) was calculated in the proximity of the kindergarten of Via Centro. These results should raise the attention of municipal authorities with regards to traffic management and urban planning, since situations of exposure that are normally underestimated may result in potentially dangerous consequences on human health. Given that the acceptable cancer risk proposed by the US EPA is between 1E-06 and 1E-04 (US EPA, 1989), the southern and northern ends of Via Centro, the northern part of Via Scuderlando and the junction of the two canyons would imply a cancer risk exceeding this acceptability range. When forbidding the circulation to pre-EURO 1 and EURO 1 vehicles, the cancer risk is reduced to 1.12E-04, at the junction between the two street canyons, and to 1.05E-04, in the vicinity of the kindergarten of Via Centro (Figure 3.12b). With the exception of these two cases, the cancer risk is everywhere lower than the upper acceptable level.

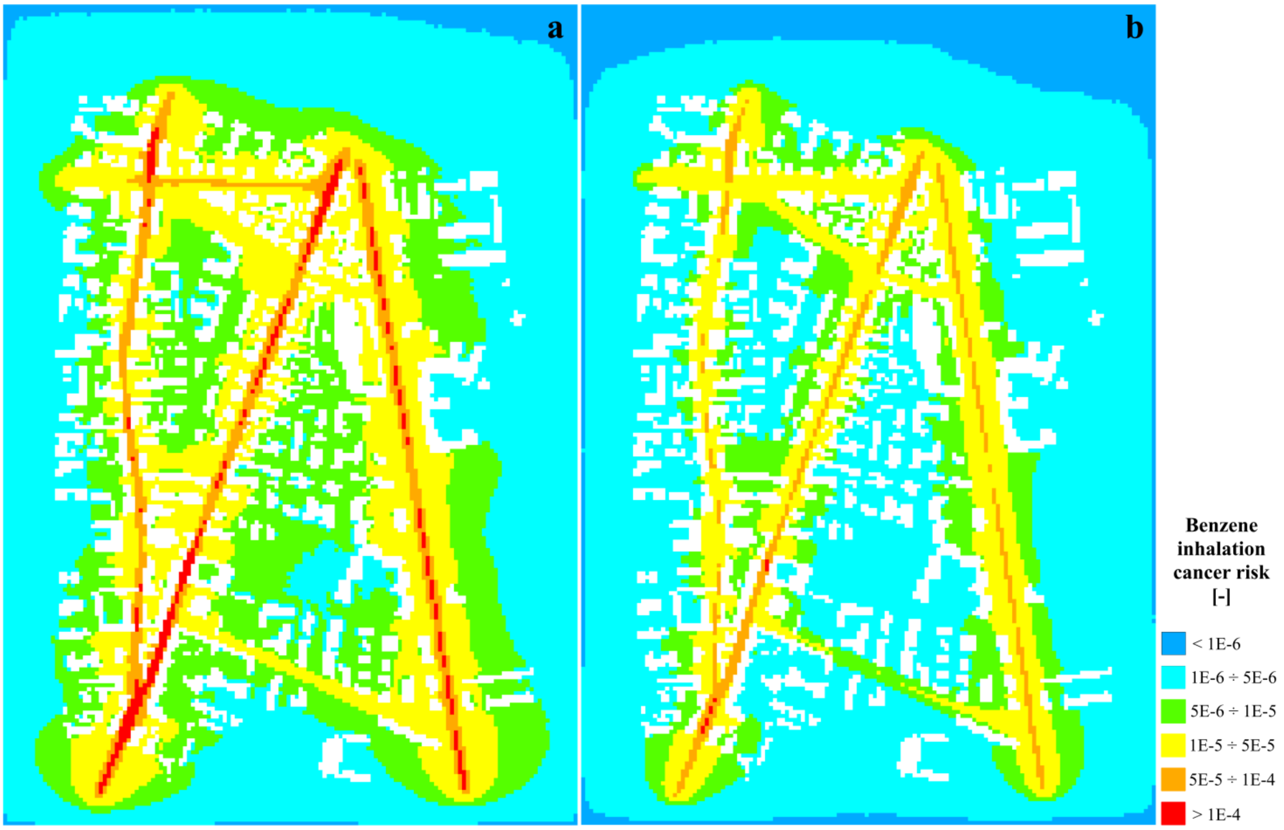

Figure 3.12: Maps of the cancer risk related to lifelong exposure to benzene concentrations induced *a)* by the whole vehicle fleet and *b)* only by the EURO 2 and latest vehicles.

3.5.4 Conclusions

The air quality simulations carried out over an urban area of Verona, characterized by street canyons and typical urban emission sources (road traffic and domestic heating), highlighted potentially critical situations of human exposure that may not be detected by the conventional network of air quality monitoring stations. As a matter of novelty, in addition to road traffic, the contribution of domestic heating in terms of NO_x was also considered. However, in spite of the effort of considering an additional sector, compared to data from air quality monitoring stations, about 35% of the contribution to NO_x concentrations is still missing, probably deriving from industrial activities in the peripheral areas.

The air quality scenarios considering restrictions to the most polluting vehicles and the adoption of enhanced hot-water heaters showed the improvements expectable from good examples of environmental policies, although the weak dispersion occurring within street canyons limits the decrease in pollutants concentration that would be expected in open areas.

In spite of being based on unavoidable approximations, the estimation of the benzene-related cancer risk gives an overview of the criticalities expected in urban street canyons and, in general, in the urban environment, where road traffic represents the dominant source of benzene. The methodology here applied provides a basis for air quality management policies, such as planning air quality monitoring campaigns, re-locating air quality stations and supporting decisions on urban planning. The latter would be especially important for the location of particularly sensitive communities, such as hospitals or schools: locating sensitive buildings far from emission sources and street canyons or in open spaces would allow reducing the risk for health. To this regard, the concept of exposure is of great interest, especially due to the fact that the current European legislation does not consider the proximity between emission sources and settled population. The estimation of the induced cancer risk is an important starting point to conduct zoning analyses and to detect the areas where a population is directly exposed to potential health risks.

4 A proposal for a regulatory limit for atmospheric deposition of PCDD/Fs

Based on: Schiavon, M., Ragazzi, M., Rada, E.C., 2013. A proposal for a diet-based local PCDD/F deposition limit. *Chemosphere* 93(8), 1639-1645. The final publication is available at Elsevier via http://dx.doi.org/10.1016/j.chemosphere.2013.08.041.

4.1 Introduction

This chapter presents the methodology and the calculations that led to the formulation of a limit value for PCDD/F deposition to soil, according to the typical diet of a target population. The same methodology is applicable to different diets and, thus, different locations, if data on the food consumption exist. The proposal for the adoption of a limit value is motivated by the absence of any regulatory limit on atmospheric deposition. Forbidding the consumption of food, directly or indirectly coming from agricultural fields or pastures that are subject to unacceptable levels of PCDD/F deposition, would preserve the food chain by contamination and, hence, would limit the human exposure. This strategy would contribute to minimize the impacts of an underestimated pathway of human exposure (the diet) at the level of the final receptor (the human body).

Due to the lipophilic properties of POPs, bioaccumulation represents the most important way of contamination by PCDD/Fs, these compounds being capable to enter the food chain. PCDD/Fs are accumulated in adipose tissues of animals and, consequently, of humans. The most important route of exposure to PCDD/Fs is food consumption, primarily dairy products, followed by cereals and vegetables, meat and fish (Eduljee and Gair, 1996). More recent studies highlighted the importance of fish and meat, which, in specific cases, contribute more than cereals and vegetables to the daily PCDD/F intake (Srogi, 2008; Zhang et al., 2013). Food contamination is primarily due to the emission of semi-volatile compounds from various sectors (*e.g.*, waste treatment, production of chemicals, metal industry, domestic heating), their subsequent deposition to soil and grass and the consequent accumulation in the food chain (Liem A.K.D. et al., 2000). Grass is the primary food for the cattle (McLachlan, 1997) and, as a consequence, their main source of PCDD/Fs. Several studies were performed to reconstruct the accumulation process of PCDD/Fs in the grass-cattle-milk/beef food chain (Prinz et al., 1993; Slob and Van Jaarsveld, 1993; Slob et al., 1995; Mclachlan, 1997; Van Lieshout et al., 2001) and to derive guide values for the atmospheric deposition to the ground, starting from the analysis of deposition samples collected in specific regions (De Fré et al., 2000; Van Lieshout et al., 2001).

The aim of this chapter is to calculate a limit value for the PCDD/F deposition, starting from the diet of people living in an Alpine region of Italy and from the WHO guide value for the TDI. The study will be carried out by assuming that the diet is entirely composed of local products. The food chain will be studied by applying some formulations presented in Lorber et al. (2000), Mclachlan (1997) and Slob and Van Jaarsveld (1993), but the chain will be run backwards with respect to the classical approach, by starting from the TDI and the consequent maximal concentration of PCDD/Fs in milk fat, running through the assimilation process of the cow and obtaining a deposition value to the ground that should not be exceeded. Afterwards, the obtained limit value will be compared with the average PCDD/F deposition measured in the same region during a monitoring campaign, in order to highlight possible criticalities. Additional calculations will be performed by considering the contribution of cereals and vegetables, due to the presence of fields in the area of study. The contribution of meat and fish will not be considered, since no fish farming is present in the area and breeding farms are dedicated to the production of milk and dairy products. In addition, as anticipated in Section 2.3.1.9, the sediment-fish-human pathway is currently lacking an appropriate food-chain model. However, indications on the methodology to estimate a PCDD/F deposition limit when considering the consumption of locally produced and meat will be presented. The main difference between this methodology and the work of (Van Lieshout et al., 2001) consists in the purpose of calculating a deposition guide value directly on the basis of the diet and the TDI, instead of deriving the guide value iteratively, starting from the deposition to obtain a target TDI. The approach proposed in this paper is then able to directly assess the overall acceptable deposition for an area.

4.2 Material and methods

In 1998 the WHO recommended a TDI of 1-4 pg WHO-TEQ kg^{-1} d^{-1} as the maximal tolerable intake on a provisional basis, but it stressed the need to reduce human intake to less than 1 pg WHO-TEQ kg^{-1} d^{-1} (Rada et al., 2011). Due to the absence of updated guide values for the TDI, this study focuses on the estimation of a limit value for the PCDD/F deposition to soil, starting from a maximal TDI of 1 pg WHO-TEQ kg^{-1} d^{-1}.

The region under investigation is the Alpine valley that is the seat of the steel plant which is the object of investigation of Sections 3.2, 3.3 and 3.4. The PCDD/F deposition to soil was kept under observation by means of the bulk deposition network described in Section 3.3.2, whose deposimeters were installed near sensitive receptors, such as a kindergarten and a primary school. The here used deposition data refer to one year of measurements (September 2010 – September 2011) taken near the primary school, located eastward with respect to the plant, about 1.2 km far from its stacks. Since this study involves the transfer of PCDD/Fs through the food chain, the measured depositions are expressed in terms of WHO-TEQ, according to the last WHO-TEF definition scheme of 2005 (Van den Berg et al., 2006) (Table 4.1).

In order to run the food chain backwards, a characterization of the typical diet for seven age classes (0-11 months, 12-35 months, 36 months – 9 years, 10-17 years, 18-64 years, 65-74 years, over 75 years) was performed, based on the European Food Safety Authority (EFSA) data about food consumption in Italy (EFSA, 2012). Realistic body weight data for each age were assumed (Table 4.2), in order to calculate the daily amount of dairy products for every year of life. The average fat content of these products (expressed in g of fat per g of product), with particular regard to dairy products of the north of Italy, is 0.037 for milk, 0.039

Table 4.1: Mean daily PCDD/F depositions to soil measured at the monitoring site from the 31st of August 2010 to the 3rd of October 2011 and mean congener composition; the deposition values are expressed according to the WHO-TEF definition scheme of 2005 (Van den Berg et al., 2006).

PCDD/F Congeners	**Depositions to soil** [pg WHO-TEQ m^{-2} d^{-1}]													**mean composition**
	2010	2010	2010	2010	2010-2011	2011	2011	2011	2011	2011	2011	2011	2011	
	31 Aug	22 Sep	14 Oct	03 Nov	24 Dec	04 Jan	01 Feb	02 Mar	08 Apr	19 May	29 Jun	09 Aug	08 Sep	[%]
	21 Sep	13 Oct	02 Nov	25 Nov	03 Jan	14 Jan	01 Mar	05 Apr	18 May	28 Jun	08 Aug	07 Sep	03 Oct	
2,3,7,8-TCDD	1.38E-02	8.48E-02	7.61E-03	2.60E-02	1.45E-02	1.45E-02	5.16E-03	4.15E-03	7.23E-03	3.54E-03	1.06E-02	6.49E-02	5.59E-03	1.70
1,2,3,7,8-PeCDD	4.12E-01	1.17E-01	7.61E-03	6.37E-01	1.45E-02	1.42E-01	3.99E-01	9.97E-03	3.20E-01	1.49E-02	7.08E-03	7.27E-02	2.07E-01	13.26
1,2,3,4,7,8-HxCDD	2.70E-03	6.95E-04	1.98E-03	6.75E-03	1.45E-03	6.47E-02	4.31E-02	3.90E-03	1.16E-03	2.26E-03	1.34E-03	1.45E-03	3.69E-03	0.66
1,2,3,6,7,8-HxCDD	1.24E-01	4.59E-03	1.67E-03	1.06E-01	4.35E-03	7.40E-02	1.09E-01	4.82E-02	7.15E-03	6.44E-03	3.61E-03	2.79E-02	4.58E-02	3.44
1,2,3,7,8,9-HxCDD	1.60E-03	6.95E-04	2.13E-03	1.06E-02	1.45E-03	5.49E-02	3.89E-02	7.97E-03	2.24E-03	3.33E-03	1.96E-01	1.03E-02	5.59E-03	1.54
1,2,3,4,6,7,8-HpCDD	9.25E-02	4.39E-02	4.24E-02	8.77E-02	1.57E-01	6.21E-02	3.62E-02	9.39E-03	3.42E-02	1.78E-02	1.08E-01	7.63E-02	2.17E-02	4.31
OCDD	5.70E-03	5.59E-03	3.55E-03	8.88E-03	2.88E-02	3.98E-03	3.19E-03	3.36E-03	4.61E-03	1.99E-03	1.98E-02	1.67E-02	5.57E-03	0.66
2,3,7,8-TCDF	2.45E-01	3.96E-01	5.93E-02	1.88E-01	3.45E-01	3.61E-01	1.14E-01	8.64E-02	7.98E-02	3.50E-02	1.54E-01	1.30E-01	8.17E-02	12.50
1,2,3,7,8-PeCDF	1.75E-02	4.75E-02	2.28E-04	8.45E-03	4.00E-02	4.94E-02	4.46E-02	8.90E-03	2.51E-03	3.44E-03	4.10E-02	4.94E-03	4.46E-02	1.43
2,3,4,7,8-PeCDF	3.06E-01	5.42E-01	7.48E-01	6.11E-01	8.97E-01	5.03E-01	3.78E-01	3.74E-03	3.01E-02	9.41E-02	4.37E-01	1.51E-01	1.43E+00	25.73
1,2,3,4,7,8-HxCDF	9.63E-02	1.54E-01	5.49E-02	1.93E-01	5.11E-01	1.88E-01	1.22E-01	1.86E-02	9.97E-03	7.15E-02	4.86E-01	4.09E-02	4.28E-01	9.92
1,2,3,6,7,8-HxCDF	2.12E-01	1.43E-01	1.16E-01	4.01E-01	1.23E-01	1.99E-01	1.36E-01	1.98E-02	2.02E-02	6.72E-02	1.34E-01	1.60E-02	2.60E-01	8.52
2,3,4,6,7,8-HxCDF	3.85E-03	1.89E-01	1.32E-01	1.71E-01	4.15E-01	3.35E-01	1.62E-01	9.05E-02	5.78E-04	8.42E-02	2.97E-01	4.94E-02	2.76E-01	11.16
1,2,3,7,8,9-HxCDF	1.69E-03	1.67E-03	1.52E-03	1.36E-02	1.45E-03	3.73E-02	1.87E-02	1.41E-03	1.16E-03	1.13E-03	1.78E-02	5.04E-03	1.44E-02	0.52
1,2,3,4,6,7,8-HpCDF	6.77E-02	3.81E-02	2.13E-02	5.68E-02	8.59E-02	6.82E-02	3.06E-02	3.17E-02	1.94E-02	3.23E-02	1.84E-01	2.52E-02	1.00E-01	4.17
1,2,3,4,7,8,9-HpCDF	4.31E-03	6.81E-04	3.06E-03	9.08E-03	7.20E-03	7.40E-03	1.05E-02	3.28E-03	3.18E-04	1.61E-03	1.42E-02	3.12E-03	1.80E-02	0.40
OCDF	7.14E-05	3.54E-04	9.13E-04	1.92E-03	2.22E-03	1.44E-03	6.29E-04	2.19E-04	1.34E-04	9.00E-04	5.27E-03	5.17E-04	3.46E-03	0.08
TOTAL	1.817	2.159	1.701	2.944	3.254	2.531	1.930	0.358	0.559	0.505	2.420	0.789	3.923	

for yoghurt, 0.305 for soft cheese, 0.290 for mature cheese, 0.285 for cream and 0.825 for butter (Gambelli et al., 1999; Mila - Milkon Alto Adige, 2013; Trentingrana, 2013). The daily fat intake is obtained by multiplying each quantity of product ingested by its fat content. To indicate the TDI related to each age, the term TDI_{bw} was introduced. The latter was calculated by multiplying the TDI (1 pg WHO-TEQ kg^{-1} d^{-1}) by the body weight of each age class. As showed in Table 4.2, the calculated TDI_{bw} is more restrictive for children, since it depends on the body weight. However, in view of the estimated long elimination half-life of PCDD/Fs, the proposed TDI should be regarded as a time-weighted average tolerable intake. If considering a mean lifetime of 80 years for the local population, the resulting average maximal PCDD/F daily intake is 59 pg WHO-TEQ d^{-1}. The average milk fat consumption for the lifetime is 29 g_{fat} d^{-1}. Dividing the average maximal intake by this value gives a maximal tolerable PCDD/F concentration of 2.056 pg WHO-TEQ g^{-1} in cow's milk fat.

According to the formulation of Slob and Van Jaarsveld (1993), already presented at Section 2.3.1.9 (Eq. 2.15), C_{mf} can be calculated as follows[8]:

$$C_{mf} = \frac{b_{mf} \cdot IR_c}{P_{mf}} \qquad \text{Eq. 4.1}$$

where IR_c is the total daily intake of PCDD/Fs by the cow and P_{mf} is the average daily production of milk fat. P_{mf} can be estimated starting from P_m (expressed in g y^{-1}), according to the relation:

$$P_{mf} = \frac{f_{f,m} \cdot P_m}{t_m} \qquad \text{Eq. 4.2}$$

where t_m is the number of milk producing days per year (Slob and Van Jaarsveld, 1993). The maximal total daily intake of PCDD/F by the cow can be obtained by combining Eq. 4.1 with Eq. 4.2:

$$IR_c = \frac{f_{f,m} \cdot P_m \cdot C_{mf}}{t_m \cdot b_{mf}} \qquad \text{Eq. 4.3}$$

where $f_{f,m}$ can be assumed as 0.044 for raw milk, C_{mf} is the previously calculated value of 2.056 pg WHO-TEQ g_{fat}^{-1} and t_m is typically 300 d y^{-1} (Slob and Van Jaarsveld, 1993). If assuming a milk production of about 7,000 L y^{-1} per cow and a milk density of 1,030 g L^{-1}, the corresponding milk production is 7.21 Mg y^{-1}. Congener-specific values for b_{mf} are listed in (McLachlan, 1997), on the basis of other previous studies (Firestone et al., 1979; Stevens and Gerbec, 1988; Olling et al., 1991; Mclachlan, 1992; Slob et al., 1995), whilst average values for b_{mf} are proposed in Kerst et al. (2004). The reported values show a high variability among the different studies. Moreover, the current approach starts from the TDI for total PCDD/Fs proposed by the WHO and no TDI values are proposed for the single congener. Thus, it was decided to follow the approach of the German guideline VDI 2310-46 and adopt a bioavailability of 0.35, peculiar to the three most toxic congeners (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF) (VDI, 2005).

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[8] The meaning of the symbols already defined can be easily recalled by consulting the Index of symbols (page xiii).

Table 4.2: Estimated mean body weight (males and females), consumption of dairy products, consequent fat intake and corresponding TDI$_{bw}$ for a 80-year lifetime (EFSA, 2012).

Age	**body weight**	**food consumption**				**total fat intake**	**TDI$_{bw}$**
		milk	fermented milk products	cream	cheese		
[yr]	[kg]	[g d^{-1}]	[g d^{-1}]	[g d^{-1}]	[g d^{-1}]	[g d^{-1}]	[pg WHO-TEQ d^{-1}]
<1	8	589	26	0	9	31	8
1	11	248	37	0	27	27	11
2	13	293	43	0	31	32	13
3	15	128	11	1	27	15	15
4	17	145	13	1	30	17	17
5	19	162	14	1	34	19	19
6	22	188	16	1	39	22	22
7	25	213	18	1	44	25	25
8	28	239	21	1	50	28	28
9	31	265	23	1	55	31	31
10	35	107	13	1	40	19	35
11	39	119	15	2	45	21	39
12	45	137	17	2	52	24	45
13	50	152	19	2	58	27	50
14	54	164	20	2	62	29	54
15	57	174	21	2	66	31	57
16	60	183	22	2	69	32	60
17	62	189	23	2	71	33	62
18	63	97	21	21	55	30	63
19	64	99	22	22	56	31	64
20	65	100	22	22	57	31	65
21	65	100	22	22	57	31	65
…	…	…	…	…	…	…	…
28	65	100	22	22	57	31	65
29	65	100	22	22	57	31	65
30	66	102	22	22	58	32	66
31	66	102	22	22	58	32	66
…	…	…	…	…	…	…	…
38	66	102	22	22	58	32	66
39	66	102	22	22	58	32	66
40	68	105	23	23	59	32	68
41	68	105	23	23	59	32	68
…	…	…	…	…	…	…	…
48	68	105	23	23	59	32	68
49	68	105	23	23	59	32	68
50	69	107	23	23	61	33	69
51	69	107	23	23	61	33	69
52	69	107	23	23	61	33	69
53	69	107	23	23	61	33	69
54	69	107	23	23	61	33	69
55	68	105	23	23	60	33	68
56	68	105	23	23	60	33	68
57	68	105	23	23	60	33	68
58	68	105	23	23	60	33	68
59	68	105	23	23	60	33	68
60	67	103	23	23	59	32	67
61	67	103	23	23	59	32	67
62	67	103	23	23	59	32	67
63	67	103	23	23	59	32	67
64	67	103	23	23	59	32	67
65	66	105	15	1	49	21	66
66	66	105	15	1	49	21	66
67	66	105	15	1	49	21	66
68	66	105	15	1	49	21	66
69	66	105	15	1	49	21	66
70	66	105	15	1	49	21	66
71	64	101	14	1	47	21	64
72	64	101	14	1	47	21	64
73	64	101	14	1	47	21	64
74	64	101	14	1	47	21	64
75	64	144	15	0	51	24	64
76	63	140	14	0	50	23	63
77	62	139	14	0	49	23	62
78	62	139	14	0	49	23	62
79	62	139	14	0	49	23	62
80	61	137	14	0	49	23	61

IR_c is the sum of the PCDD/F daily intake from grass consumption ($IR_{c,g}$) and from soil ingestion by the cow ($IR_{c,s}$). The first one depends on the PCDD/F deposition on the grass (seen as the total deposition D multiplied by the fraction c_g of surface covered by grass), the average area (A) of meadow grazed by one cow during one month and t_r is the average number of days per month (Slob and Van Jaarsveld, 1993), according to the following relation:

$$IR_{c,g} = \frac{A \cdot c_g \cdot D}{t_r} \qquad \text{Eq. 4.4}$$

where A is approximately 3,000 m^2 $month^{-1}$, c_g is assumed to be 0.9 and t_r is 30.4 d $month^{-1}$.

The deposition to grass should be corrected to account for runoff processes due to the rain. In the absence of information, no wash-off parameters were taken into account. Thus, such an approach leads to precautionary results. Analogously to accidental soil ingestion by humans (Eq. 2.9), $IR_{c,s}$ depends on the amount of soil ingested ($I_{c,s}$) and C_s:

$$IR_{c,s} = I_{c,s} \cdot C_s \qquad \text{Eq. 4.5}$$

According to Slob and Van Jaarsveld (1993), $I_{c,s}$ can be assumed as equal to 225 g d^{-1}. An expression for C_s was defined in Eq. 2.8. The other parameters of such expression were taken as equal to the values adopted by Lorber et al. (2000), defined in Section 2.3.1.9.

In order to obtain a deposition limit value for the future years, C_s was calculated on a temporal horizon of 30 y, by assuming D_{LT} equal to the average annual deposition measured during the monitoring campaign, which is 510 pg WHO-TEQ m^{-2} y^{-1}. Using this value in Eq. 2.8 implies the assumption that a mean PCDD/F deposition of 510 pg WHO-TEQ m^{-2} will be encountered annually for the whole reference period of 30 y.

IR_c can now be expressed as a function of the total deposition D:

$$IR_c = IR_{c,g} + IR_{c,s} = \frac{A \cdot c_g \cdot D}{t_r} + I_{c,s} \cdot C_s \qquad \text{Eq. 4.6}$$

Thus, the deposition can be calculated as follows:

$$D = \frac{t_r}{A \cdot c_g} \left(\frac{f_{f,m} \cdot P_m \cdot C_{mf}}{t_m \cdot b_{mf}} - I_{c,s} \cdot C_s \right) \qquad \text{Eq. 4.7}$$

By attributing the maximal PCDD/F concentration value in milk fat to C_{mf}, D represents a limit value for the PCDD/F deposition on a monthly basis.

According to Eduljee and Gair (1996), the consumption of cereals and vegetables represents the second most important route of PCDD/F intake. The uptake by plants occurs through three main pathways: interaction between soil and root system, particulate deposition and dry gaseous deposition to above-ground shoots, the first two playing a minor role with respect to the latter (Harrad and Smith, 1997; UK Environment Agency, 2009).

As presented in Section 2.3.1.9, the contribution of root uptake ($C_{p,r}$) can be calculated by means of the soil-to-plant *BCF*s used in the CLEA plant uptake models (UK Environment Agency, 2009) and in Huelster et al. (1994) (Table 4.3). The *BCF*s refer to the following plant groups: green vegetables, root vegetables, tuber vegetables, herbaceous fruits and tree fruits. The PCDD/F concentration into the plant is calculated by multiplying the *BCF*s by the PCDD/F concentration in soil. To compare the contribution of these products with dairy products, C_s will be calculated from Eq. 2.8, by using the long-term deposition value measured for the case study (510 pg WHO-TEQ m^{-2} y^{-1}).

The total PCDD/F concentration into the plant due to the contribution of dry gaseous deposition to aboveground shoots and leaves ($C_{p,dg}$) can be estimated through the following formulations (Junge, 1977; Bidleman, 1988; Lorber et al., 1994; Harrad and Smith, 1997), which is analogous to the congener-specific formulation presented in Eq. 2.11:

$$C_{p,dg} = \frac{B_{vpa} \cdot f_v \cdot C_a}{\rho_a} \qquad \text{Eq. 4.8}$$

where f_v is the fraction of total air concentration in vapour phase at 293 K, which is complementary to the fraction of total air concentration sorbed to particulates at the same temperature (f_p). The latter is obtained as follows:

$$f_p = \frac{c \cdot S_t}{P_s + c \cdot S_t} \qquad \text{Eq. 4.9}$$

where P_s is the saturation vapour pressure of sub-cooled liquid and the remaining parameters assume the same values proposed in Section 2.3.1.9. C_a can be calculated by starting from congener-specific deposition velocities ($V_{d,j}$) and multiplying each of them by the respective measured deposition (Meneses et al., 2002). The congener-specific parameters ($V_{d,j}$, $BCF_{p,j}$, $B_{vpa,j}$) and the calculated congener-specific values for C_s, C_a, P_s and f_p are presented in Table 4.3, according to the WHO-TEF definition scheme of 2005. Since *BCF*s are provided for the single congeners, a C_s value for each congener was calculated considering the respective measured long-term total deposition value.

The total PCDD/F concentration into the plant due to the contribution of particulate deposition ($C_{p,p}$) can be obtained by applying Eq. 2.12 and assuming the same values of each parameter presented in Section 2.3.1.9. Finally, the accumulation in fruit ($C_{p,f}$), due to the uptake from air and the stem, can be estimated by means of the tree model developed by Trapp (2007).

Table 4.3: Congener-specific parameters adopted for calculating the contribution of root uptake, dry gaseous and particulate depositions to the PCDD/F concentration of vegetables (Huelster et al., 1994; Harrad and Smith, 1997; Meneses et al., 2002; UK Environment Agency, 2009); the WHO-TEF scheme adopted refers to the last revision of 2005 (Van den Berg et al., 2006).

PCDD/F Congeners	**WHO-TEF**	**v_d**	**C_s**	**C_a**	**BCF**					**B_{vpa}**	**P_l**	**f_p**	**f_v**
					green veg.	root veg.	tuber veg.	tree fruit	herb. fruit				
	[-]	[m s^{-1}]	[pg WHO-TEQ g^{-1}]		[-]					[-]	[atm]	[-]	[-]
2,3,7,8-TCDD	1	0.069	1.67E-03	2.35E-04	2.59E-05	2.38E-04	1.72E-04	9.33E-08	1.02E-02	1.43E+05	7.16E-10	4.54E-01	5.46E-01
1,2,3,7,8-PeCDD	1	0.091	1.30E-02	1.78E-04	4.68E-06	9.28E-05	6.60E-05	8.57E-09	1.02E-02	2.78E+05	2.13E-10	7.37E-01	2.63E-01
1,2,3,4,7,8-HxCDD	0.1	0.166	6.43E-04	9.74E-05	7.36E-07	3.62E-05	2.51E-05	6.51E-10	6.67E-02	1.06E+06	4.68E-11	9.27E-01	7.29E-02
1,2,3,6,7,8-HxCDD	0.1	0.166	3.37E-03	9.74E-05	7.36E-07	3.62E-05	2.51E-05	6.51E-10	6.67E-02	1.06E+06	2.18E-11	9.65E-01	3.54E-02
1,2,3,7,8,9-HxCDD	0.1	0.166	1.51E-03	9.74E-05	7.36E-07	3.62E-05	2.51E-05	6.51E-10	6.67E-02	1.06E+06	1.14E-11	9.81E-01	1.88E-02
1,2,3,4,6,7,8-HpCDD	0.01	0.291	4.22E-03	5.56E-05	1.01E-07	1.41E-05	9.43E-06	4.03E-11	1.60E-03	8.09E+05	1.23E-11	9.80E-01	2.02E-02
OCDD	0.0003	0.426	6.45E-04	3.80E-05	1.21E-08	5.47E-06	3.55E-06	2.00E-12	2.90E-04	2.01E+07	1.29E-12	9.98E-01	2.17E-03
2,3,7,8-TCDF	0.1	0.150	1.23E-02	1.08E-04	1.38E-04	6.54E-04	4.53E-04	9.73E-07	7.54E-03	1.90E+05	1.45E-09	2.90E-01	7.10E-01
1,2,3,7,8-PeCDF	0.03	0.178	1.40E-03	9.09E-05	3.11E-05	2.67E-04	1.87E-04	1.19E-07	8.27E-03	1.90E+05	4.26E-10	5.83E-01	4.17E-01
2,3,4,7,8-PeCDF	0.3	0.178	2.52E-02	9.09E-05	3.11E-05	2.67E-04	1.87E-04	1.19E-07	8.27E-03	1.90E+05	2.54E-10	7.01E-01	2.99E-01
1,2,3,4,7,8-HxCDF	0.1	0.178	9.72E-03	9.09E-05	6.20E-06	1.09E-04	7.54E-05	1.26E-08	5.51E-03	3.48E+05	3.79E-11	9.40E-01	5.99E-02
1,2,3,6,7,8-HxCDF	0.1	0.178	8.35E-03	9.09E-05	6.20E-06	1.09E-04	7.54E-05	1.26E-08	5.51E-03	3.48E+05	7.13E-11	8.93E-01	1.07E-01
2,3,4,6,7,8-HxCDF	0.1	0.178	1.09E-02	9.09E-05	6.20E-06	1.09E-04	7.54E-05	1.26E-08	5.51E-03	3.48E+05	4.04E-11	9.36E-01	6.35E-02
1,2,3,7,8,9-HxCDF	0.1	0.178	5.05E-04	9.09E-05	6.20E-06	1.09E-04	7.54E-05	1.26E-08	5.51E-03	3.48E+05	4.16E-11	9.35E-01	6.53E-02
1,2,3,4,6,7,8-HpCDF	0.01	0.107	4.09E-03	1.51E-04	1.12E-06	4.45E-05	3.00E-05	1.17E-09	1.74E-03	1.04E+06	2.69E-11	9.57E-01	4.32E-02
1,2,3,4,7,8,9-HpCDF	0.01	0.107	3.96E-04	1.51E-04	1.12E-06	4.45E-05	3.00E-05	1.17E-09	1.74E-03	1.04E+06	1.51E-11	9.75E-01	2.48E-02
OCDF	0.0003	0.065	8.26E-05	2.49E-04	1.74E-07	1.81E-05	1.19E-05	8.68E-11	8.70E-04	2.97E+06	1.25E-12	9.98E-01	2.09E-03

4.3 Results and discussion

4.3.1 Verification of the main intake pathway

To verify the main role of dairy products in the exposure to dioxin, the daily PCDD/F intake was calculated for cow's milk consumption, by using the data about the Italian diet and the deposition measured from September 2010 to September 2011 and following the approaches of Slob and Van Jaarsveld (1993) and Lorber et al. (2000). The PCDD/F concentration in milk fat was calculated from Eq. 4.3, Eq. 4.2 and Eq. 4.1, applied in cascade, resulting in 1.25 pg WHO-TEQ g^{-1}. The PCDD/F intake from dairy products related to the measured deposition (1.40 pg WHO-TEQ m^{-2} d^{-1}) is 0.61 pg WHO-TEQ kg^{-1} d^{-1}. Similarly, the contribution of cereals and vegetables to the daily PCDD/F intake was estimated. Since cereals and vegetables are generally more present in the Italian and South-European diet in comparison with the rest of Europe, it is necessary to clarify the role of these products and verify if their consumption does not involve a greater PCDD/F intake. A total value of $C_{p,r}$ was then calculated for every plant group considered. By applying Eq. 4.8, Eq. 4.9 and Eq. 2.12, $C_{p,dg}$ and $C_{p,p}$ were also obtained. Finally, the accumulation in fruit ($C_{p,f}$) was calculated according to Trapp (2007). For each congener, $C_{p,f}$ was two orders of magnitude lower than $C_{p,dg}$ and almost one order lower than $C_{p,p}$. In addition, $C_{p,r}$ was even lower than $C_{p,f}$ for green vegetables, tubers, root vegetables and tree fruit. $C_{p,r}$ was of the same order of magnitude of $C_{p,f}$ only for herbaceous fruit (Table 4.4).

The total PCDD/F concentrations in vegetables were then calculated as follows: the contribution of the root uptake was considered for every group, the accumulation in fruit was taken into account only for tree fruit, whilst the contribution of dry gaseous and particulate depositions were considered only for green vegetables and herbaceous fruit. By using the statistics on the Italian diet (EFSA, 2012), the PCDD/F daily intake was calculated by multiplying the mass of vegetables ingested by the respective PCDD/F content. The resulting percent contribution of vegetables (including cereals and fruit) and dairy products is 17% and 83% over the lifetime, respectively, confirming the main role of dairy products in the daily absorption of PCDD/Fs.

4.3.2 Deposition limit proposal and comparison with the measured deposition

To investigate the roles of the daily intake from grass consumption ($IR_{c,g}$) and soil ingestion ($IR_{c,s}$), these two terms were calculated separately through Eq. 4.4, Eq. 4.5 and Eq. 2.8 on the basis of the measured deposition: $IR_{c,s}$ turned out to be three orders of magnitude lower than $IR_{c,g}$, thus the total intake IR_c can be assumed as equal to $IR_{c,g}$. As a consequence, Eq. 4.7 can be simplified as follows:

$$D = \frac{t_r \cdot f_{f,m} \cdot P_m \cdot C_{mf}}{A \cdot c_g \cdot t_m \cdot b_{mf}} \qquad \text{Eq. 4.10}$$

By applying this formulation, the resulting limit value for PCDD/F deposition was 2.30 pg WHO-TEQ m^{-2} d^{-1}. This value is 68% the deposition limit proposed by Van Lieshout et al. (2001), which is 3.4 pg WHO-TEQ m^{-2} d^{-1}, and 58% the target value of 4 pg WHO-TEQ m^{-2} d^{-1} for deposition of PCDD/Fs and dioxin-like PCBs established by the German Committee for Pollution Control (LAI). For the case study, the measured deposition (1.40 pg WHO-TEQ m^{-2} d^{-1}) is below the resulting limit value. The latter should be intended as a threshold value below which the population can be considered subject to a low PCDD/F exposure, since the present study started from a TDI of 1 pg WHO-TEQ m^{-2} kg^{-1} d^{-1}, that is the lower bound of the range suggested by the WHO (1-4 pg WHO-TEQ m^{-2} kg^{-1} d^{-1}). Therefore, a 4 times higher deposition limit can represent a threshold over which an investigation about the PCDD/F content of the locally produced food becomes opportune.

According to the approach presented here, the obtained deposition value is calculated only with respect to the consumption of dairy products, by assuming that local products represent 100% of the diet for the region. Should also cereals and vegetables be subject to the maximal calculated deposition, the total PCDD/F intake would be higher than 1 pg WHO-TEQ kg^{-1} d^{-1}. Since this approach can be applied also at regional scale, thus including more emission sources, the possibility exists that the maximal PCDD/F deposition can affect also cereals and vegetables. The maximal deposition limit can then be re-calculated by assuming that also cereals and vegetables are 100% locally consumed. In order to reach the target TDI, the resulting deposition be-

Table 4.4: Congener-specific concentrations related to different contributions: root uptake ($C_{p,r}$), dry gaseous deposition ($C_{p,dg}$), particulate deposition ($C_{p,p}$) and accumulation in tree fruit ($C_{p,f}$); concentrations are expressed in accordance with the WHO-TEF definition scheme of 2005 (Van den Berg et al., 2006).

PCDD/F Congeners	$C_{p,r}$ green veg.	 root veg.	 tuber veg.	 tree fruit	 herb. fruit	$C_{p,dg}$	$C_{p,p}$	$C_{p,f}$
				[pg WHO-TEQ g^{-1}]				
2,3,7,8-TCDD	4.33E-08	3.98E-07	2.87E-07	1.56E-10	1.70E-05	1.54E-02	1.40E-04	5.32E-04
1,2,3,7,8-PeCDD	6.08E-08	1.21E-06	8.58E-07	1.11E-10	1.33E-04	1.10E-02	1.09E-03	4.15E-04
1,2,3,4,7,8-HxCDD	4.73E-10	2.33E-08	1.61E-08	4.19E-13	4.29E-05	6.33E-03	5.39E-05	2.88E-05
1,2,3,6,7,8-HxCDD	2.48E-09	1.22E-07	8.46E-08	2.19E-12	2.25E-04	3.07E-03	2.83E-04	2.88E-05
1,2,3,7,8,9-HxCDD	1.11E-09	5.47E-08	3.79E-08	9.84E-13	1.01E-04	1.63E-03	1.27E-04	1.15E-04
1,2,3,4,6,7,8-HpCDD	4.27E-10	5.96E-08	3.98E-08	1.70E-13	6.76E-06	7.64E-04	3.54E-04	1.82E-05
OCDD	7.81E-12	3.53E-09	2.29E-09	1.29E-15	1.87E-07	1.39E-03	5.41E-05	1.33E-05
2,3,7,8-TCDF	1.69E-06	8.01E-06	5.55E-06	1.19E-08	9.24E-05	1.22E-02	1.03E-03	1.95E-04
1,2,3,7,8-PeCDF	4.35E-08	3.73E-07	2.62E-07	1.66E-10	1.16E-05	6.05E-03	1.17E-04	1.32E-04
2,3,4,7,8-PeCDF	7.84E-07	6.73E-06	4.72E-06	3.00E-09	2.09E-04	4.34E-03	2.11E-03	8.11E-05
1,2,3,4,7,8-HxCDF	6.03E-08	1.06E-06	7.33E-07	1.22E-10	5.36E-05	1.59E-03	8.15E-04	5.09E-05
1,2,3,6,7,8-HxCDF	5.18E-08	9.11E-07	6.30E-07	1.05E-10	4.60E-05	2.84E-03	7.00E-04	5.09E-05
2,3,4,6,7,8-HxCDF	6.78E-08	1.19E-06	8.25E-07	1.38E-10	6.03E-05	1.69E-03	9.17E-04	9.61E-05
1,2,3,7,8,9-HxCDF	3.13E-09	5.50E-08	3.81E-08	6.36E-12	2.78E-06	1.74E-03	4.23E-05	5.42E-05
1,2,3,4,6,7,8-HpCDF	4.58E-09	1.82E-07	1.23E-07	4.79E-12	7.12E-06	5.71E-03	3.43E-04	3.68E-05
1,2,3,4,7,8,9-HpCDF	4.44E-10	1.76E-08	1.19E-08	4.64E-13	6.90E-07	3.27E-03	3.32E-05	5.06E-05
OCDF	1.44E-11	1.49E-09	9.83E-10	7.17E-15	7.19E-08	1.30E-03	6.92E-06	2.06E-05
TOTAL	2.82E-06	2.04E-05	1.42E-05	1.57E-08	1.01E-03	8.03E-02	8.22E-03	1.92E-03

comes lower than the previously calculated value and, precisely, equal to 1.91 pg WHO-TEQ m^{-2} d^{-1} (83% of the previously calculated limit). This new value represents an even more precautionary limit, which is, however, still higher than the mean annual deposition of the region.

Since the local breeding farms are dedicated to the production of milk, no meat-based food is produced locally. However, whereas the consumption of locally produced meat occurs, the PCDD/F deposition limit value can be corrected by applying the same approach followed when considering cereals and vegetables in addition to dairy products: by applying the classical approach, carry-over factors for PCDD/Fs in animal fat tissues can be used to calculate the PCDD/F daily intake by the humans, starting from the measured deposition and the local diet; the percent contribution of each food category (dairy products, cereals and vegetables, and meat) to the daily intake can be calculated; the new percent contribution of dairy products, multiplied by the TDI, provides the new TDI for the calculation of the deposition limit.

4.4 Conclusions

A novel approach was implemented to derive a limit value for the PCDD/F deposition to soil, starting from the diet of a region located in the north of Italy. The calculation was carried out by adapting existing models and running them backwards with respect to their original formulation. Contrarily to previous studies, the novelty of this approach consists in the calculation of a deposition guide value directly on the basis of the diet and the TDI, instead of deriving the guide value by iterations.

A deposition value of 2.30 pg WHO-TEQ m^{-2} d^{-1} was obtained by assuming the consumption of 100% locally produced dairy products (the highest contributors to the transfer of PCDD/Fs to humans), thus deriving from cattle exposed to the maximal deposition. The average PCDD/F deposition measured during the monitoring campaign in a selected site was 1.40 pg WHO-TEQ m^{-2} d^{-1}, thus lower than the resulting limit value.

The comparison between the contributions of dairy products and cereals, vegetables and fruit to the PCDD/F intake confirms that milk-derived products play a major role in the exposure to dioxins. A more precautionary deposition limit value (1.91 pg WHO-TEQ m^{-2} d^{-1}) was obtained by considering also the consumption of locally produced cereals and vegetables. The inclusion of cereals and vegetables represents an additional matter of novelty, since PCDD/F deposition guide values have been estimated only with regards to dairy products until now. Considering the contribution of the consumption of locally produced meat, whereas occurring, would lead to a more stringent deposition limit value.

5 Proposals for improved design criteria for MBTs of solid waste

5.1 Summary

As mentioned in Chapter 2, aerobic MBTs of solid waste may be responsible for the release of hazardous air pollutants and odorants in the atmosphere. This is mainly ascribed to the possible presence of contaminants in the organic fraction and to the high emission fluxes involved. However, the impact of MBTs is case-dependent and the considerations on a plant cannot be generalized. The impacts are also influenced by the effluent temperature, the aeration mode (continuous or discontinuous) and the APC strategies adopted. Contrarily to MSW incinerators, which optimize the dispersion in the atmosphere through the adoption of high chimneys, the effluents of MBTs are usually treated by biofilters located at ground level and this may negatively affect the dispersion of the plume in the atmosphere.

This chapter focuses on a critical analysis on biofilters applied to treat VOC-contaminated streams at low concentration, at the outlet of MBTs of solid waste. Specifically, two kinds of biotechnologies are here compared for a better design of air treatment lines: biofilters and BTFs. Considerations drawn from two publications carried out during this research are here reported (Ragazzi et al., 2014a; Schiavon et al., 2015b). In order to present the operation principles and the benefits offered by biotrickling filtration, a detailed review on BTFs is reported (Schiavon et al., 2015c), object of a recent publication produced during this doctoral research.

5.2 The use of quality parameters for a correct design of MBT plants in agricultural areas

Based on: Ragazzi, M., Rada, E.C., Schiavon, M., Torretta, V., 2014. Unconventional parameters for a correct design of waste biostabilization plants in agricultural areas. *Mitteilungen Klosterneuburg Rebe und Wein, Obstbau und Früchteverwertung* 64(6), 1-13.

5.2.1 Introduction

The application of MBTs and, especially, biostabilisation is particularly interesting when thought in areas with agricultural vocation. The use of the organic fraction can transform the waste to be disposed in a potential resource. In this sense, in the context of agricultural activities, biological processes have considerable importance for the treatment of waste, where the presence of the organic fraction has a very high percentage. First, anaerobic digestion, especially if it manages to combine a stream originating from livestock or related to the food industry, considers many alternatives on the input matrices (Baroň and Bábíková, 2011; Callegari et al., 2013; Rada et al., 2013b; Martinez et al., 2014). Similarly, aerobic processes (Rada et al., 2014b) can have a big interest, especially where the production of compost is compatible with the market availability to accept and use it. These systems have significant potential to be applied in any context, but are much more interesting when applied in agricultural contexts. Indeed the theme of this work, which relates to the release of PCDD/Fs from MBTs, in this case the biostabilisation of MSW, is particularly important because the depositions on the soil have implications on the food chain linked to activities such as animal husbandry. Thus, the issue addressed is particularly timely and important in an agricultural context (that is a typical location for this kind of plant).

MBT plants are considered as being a less harmful form of waste treatment for the environment. However, there are still environmental and health issues, such as the formation of odours, aerosols, noise, and the management of waste from the treatment process (Sironi et al., 2006; Ragazzi et al., 2011; Montejo et al., 2013). The aim of this work is to identify the environmental impact of MSW biostabilisation plants, in terms of PCDD/F deposition to soil.

MBTs are generally not governed by specific national regulations on PCDD/Fs (Rada et al., 2006). That justifies a lack of focus on the environmental consequences of this type of technical application. Only German and Austrian regulations set a limit of 0.1 ng I-TEQ Nm^{-3} for stack concentrations of PCDD/Fs from these processes, which is the limit established in Italy and, in general, in Europe for urban waste incineration plants (Lombardi et al., 2013). Considering these two treatment techniques on the same level is conceptually mistaken. In the case of MBTs, PCDD/F emissions into the atmosphere can have an impact on the local environment even higher than the one of a modern incinerator, both because of the high process air flow rate and because the systems used to clean the process air, including biofilters, are often located at a low height and work at low temperatures with a slower output velocity, which subsequently impacts on the dilution within the atmosphere.

This section is thus intended to clarify the role of various configurations of biofilters and a regenerative thermal oxidizer (RTO) applied to the biostabilisation of urban waste in terms of emissions and dispersion of PCDD/Fs into the atmosphere. This way, new design criteria can be proposed. Dispersion simulations were performed using the AERMOD advanced Gaussian model and the impact of the atmospheric deposition to the soil was assessed. A flat area characterized by the absence of strong winds was chosen. The cancer risk deriving from exposure to the emitted PCDD/Fs was included in the study. The introduction of a set of quality parameters that link the deposition values with their level of toxicity was used to compare the two removal technologies proposed.

5.2.2 Material and Methods

5.2.2.1 Basic data

The simulation site of the plant was based on a province in northern Italy, with climate conditions of a low land, a catchment area of about 870,000 inhabitants and an advanced management of urban waste collection. Starting with real data on the separate waste collection, the flows of the non-separated waste produced were calculated. The estimated flow for the proposed biostabilisation plant was then obtained. On the basis of an efficient selective collection (SC) and of a total of approximately 446,000 t y^{-1} of MSW, the residual MSW corresponds generally to approximately 35.5%, that is, 158,330 t y^{-1}. A biostabilisation plant is capable of treating only the undersieve of residual MSW, equal to about 30% of the total, which consists primarily in food waste and green matter, plus a percentage of other classes of waste with a fine granulometry (from the study of the waste classes, the average percentage of food and green waste, with respect to the residual MSW, was 23.4%; thus, the undersieve for biostabilisation was estimated to be about 30% of the plant input). The resulting design capacity of the proposed biostabilisation plant was assumed to be equal to 47,500 t y^{-1}.

5.2.2.2 Emissions produced

Two types of removal technologies applied to the gaseous emissions were considered: a biofilter and an RTO.

For the biofilter simulations, a rectangular configuration was considered, with horizontal dimensions of 15 m × 95 m and a resulting area of 1,425 m^2. The emission factor at the output of a biofilter, after biostabilisation, can be assumed to be equal to 40 pg I-TEQ kg^{-1} for waste with a high PCDD/F concentration (Rada et al., 2011).

The mass flow obtained was $1.91 \cdot 10^9$ pg I-TEQ y^{-1} (63 pg I-TEQ s^{-1}). The volumetric load of the biofilter was assumed to be equal to 60 $m^3\ m^{-2}\ h^{-1}$, following the indications of Devinny (1999). From the dimensions thus obtained, the flow of pollutants per unit of area was 44 fg I-TEQ $m^{-2}\ s^{-1}$. The velocity and temperature of the outgoing flow were 1.7 cm s^{-1} and 35 °C, respectively. Regarding the release height, two possible configurations were taken into account: the first one considered the biofilter located at ground level and the height of the emissions was set at 2 m above the ground. The second option considered the treatment system (biofilter) located on the roof of the building. Assuming that industrial buildings are usually about 15 m in height, the overall height established for the PCDD/F emissions was 17 m.

For the RTO, an emission factor of 2-8 pg I-TEQ kg^{-1} of waste was suggested in a previous study (Rada et al., 2006). For the present study, in order to obtain precautionary results, the upper limit (8 pg I-TEQ kg^{-1}) was adopted as the emission factor for the RTO. The resulting mass flow of PCDD/Fs from the stack was 13 pg I-TEQ s^{-1}. For the simulations, the height of the stack was set at 25 m, the temperature of the flow from the stack was assumed to be 320 K, the velocity of the off-gas was 10 m s^{-1} and the internal diameter of the stack was 1.2 m.

5.2.2.3 Dispersion model

The dispersion model adopted in this study is the American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD), a Gaussian dispersion model to determine the concentration of pollutants in the atmosphere (US EPA, 2009). Many Gaussian models use the classic diffusion expression to calculate the concentration field (Cimorelli et al., 2004). Rather than rigorously adhering to the equation, AERMOD uses expressions that have been proven to be closer to the real situation, derived after suitable revisions.

In the stable boundary layer, AERMOD considers the distribution of concentrations on both the vertical and horizontal planes to be Gaussian; however, in the Convective Boundary Layer (CBL), only the horizontal distribution is assumed to be Gaussian, while a double-Gaussian distribution is assumed for the vertical plane (Stull, 1988).

Furthermore, AERMOD considers the lofting of the plume, by assessing the possibility that a source near the top of the CBL emits pollutants that are warmer than the atmosphere, which will therefore be subject to buoyancy, and describes their subsequent return as a result of being dragged into the convective motions.

The simulations carried out include a square Cartesian grid, with receptors on the ground at every node. The areal (biofilter) or point source (RTO) is always positioned at the centre of the calculation domain. The grid has different dimensions, depending on whether the biofilter or the RTO is considered; for the biofilter, the area of interest is 3 km × 3 km and the receptors are located 20 m away from each other (151×151 receptors). For the RTO simulations, a larger area is analysed (4 km × 4 km), but the grid is wider, with nodes every 40 m (101×101 receptors). These differences stem from the fact that, in the case of the biofilter, the transportation of PCDD/Fs is affected primarily by the quantity of motion, while the vertical orientation is minimal (dense grid). In the case of RTO, the dispersion is confined to a greater height, thanks also to plume rise, and, consequently, the dilution volume is bigger, with a larger area of influence.

Meteorological data from an Italian surface weather station were used, including temperature, relative humidity, solar radiation, precipitation, wind direction and intensity and pressure. The data collected refer to the whole 2009. A profile of temperature, wind direction and wind intensity was used, measured by a radio sounding and SODAR (Sound Detection and Ranging).

The height of the mixing layer due to the convective motions within the CBL was calculated using the AERMOD Meteorological pre-processor (AERMET), a prognostic meteorological model. AERMET calculates the planetary boundary layer (PBL) parameters required by AERMOD to extrapolate profiles of wind, temperature and turbulence. AERMET estimates the Monin–Obukhov length, the surface friction velocity, the surface roughness, the surface heat flux and the convective scaling velocity according to the formulations of Venkatram (1980) and Panofsky and Dutton (1984). The stability of the PBL is defined by the sign of the surface heat flux (positive or negative, respectively). AERMET also estimates the vertical profile of the temperature and wind, irrespectively of whether or not an upper air sounding is provided. In the study area, stable (class 6: 34%), neutral (class 4: 21%) and then moderately unstable and stable atmosphere (classes 2 and 3: both 17%) conditions prevail. Very unstable (class 1: 6.6%) and slightly unstable atmosphere conditions (class 5: 4.5%) appear much less frequently.

5.2.2.4 Definition of quality parameters

The deposition guide value established in 2001 in Belgium by the Flemish Institute for Technological Research (VITO) (Cornelis et al., 2007) is 3.4 pg I-TEQ $m^{-2}d^{-1}$ (1240 pg I-TEQ $m^{-2}y^{-1}$) and corresponds to the lowest bound of the PCDD/F TDI proposed by the WHO (Van Lieshout et al., 2001). According to the hypothesis that the plant contributes to a deposition equal to the guide value, without taking into account the background levels, the deposition achieved can be defined as *TDI 100%*. This value is the first quality parameter to assess the local impacts of a facility/plant on its surrounding areas.

In order to assess whether the introduction of a new MSW treatment plant would have a significant environmental impact and, thus, to identify the possible mitigation measures, a criterion of significance can be adopted. This criterion analyses whether specific thresholds will be reached or exceeded and identifies a possible unacceptable situation based on design, technological and environmental criteria. An impact can be assumed as significant if the estimate of its contribution to the existing situation leads to an increase in the pollution levels higher than 5% of *TDI 100%* (Rada et al., 2011), that is, by 60 pg I-TEQ m^{-2} y^{-1}. This quality parameter can be named as *TDI 5%.*

The cancer risk corresponding to a continuous exposure to the TDI can be calculated by Eq. 2.1 with the adoption of the SF_{oral} proposed by the US EPA for the two most toxic congeners (2,3,7,8-TCDD and 1,2,3,7,8-PeCDD), equal to 1.3E+05 (mg kg^{-1} d^{-1})$^{-1}$ (US EPA, 2014). In fact, the product $C{\cdot}E$ corresponds to the average daily intake. Therefore, the TDI corresponds to a $1.3{\cdot}10^{-4}$ cancer risk. It is worth remarking that the concept of TDI is related to non-cancer effects (Section 2.3.1.4). In this case, the TDI is only taken as a reference value to link an intake rate value (the TDI itself) with a known deposition value (the VITO guide value). This way, the cancer risk corresponding to a deposition of 3.4 pg I-TEQ $m^{-2}d^{-1}$ is known ($1.3{\cdot}10^{-4}$) and this makes possible to obtain the PCDD/F deposition value corresponding to the acceptable cancer risk of 10^{-6}, resulting in 0.026 pg I-TEQ m^{-2} d^{-1} (9.5 pg I-TEQ m^{-2} y^{-1}). This value can be named as *TDI* 10^{-6} and represents a more stringent quality parameter with respect to the previous two.

5.2.3 Results and discussion

The total annual deposition, expressed as the sum of the dry and wet deposition, in pg I-TEQ m^{-2} y^{-1}, was calculated by AERMOD for the three configurations proposed: biofilter with a release height at 2 m above the ground, biofilter with release height at 17 m above the ground and the RTO (stack height: 25 m). The biofilter was represented by an aerial source, whilst the RTO was represented by a point source. Of all the cases considered, the biofilter at ground level is the worst solution. In this case, the maximal deposition value (4 ng I-TEQ m^{-2} y^{-1}) was found at a distance of 5 m from the biofilter, which dropped to less than 100 pg I-TEQ m^{-2} y^{-1} at about 500 m from the plant (Figure 5.1).

From an environmental point of view, positioning the biofilter above the roof of the building is a better solution if considering the impacts in the vicinity of the plant, where the maximal deposition is about 820 pg I-TEQ m^{-2} y^{-1} (Figure 5.2). However, the impact at a distance of about 1 km is similar to the one obtained by the previous configuration. The situation significantly improves with the RTO: the maximal deposition, found in the immediate vicinity of the plant, is lower than the first configuration by two orders of magnitude (Figure 5.3). Thus, the RTO seems the best solution for lowering the PCDD/F impact. Indeed, biofilters have a very slow flow, governed by the momentum, which creates more critical conditions near the emission area.

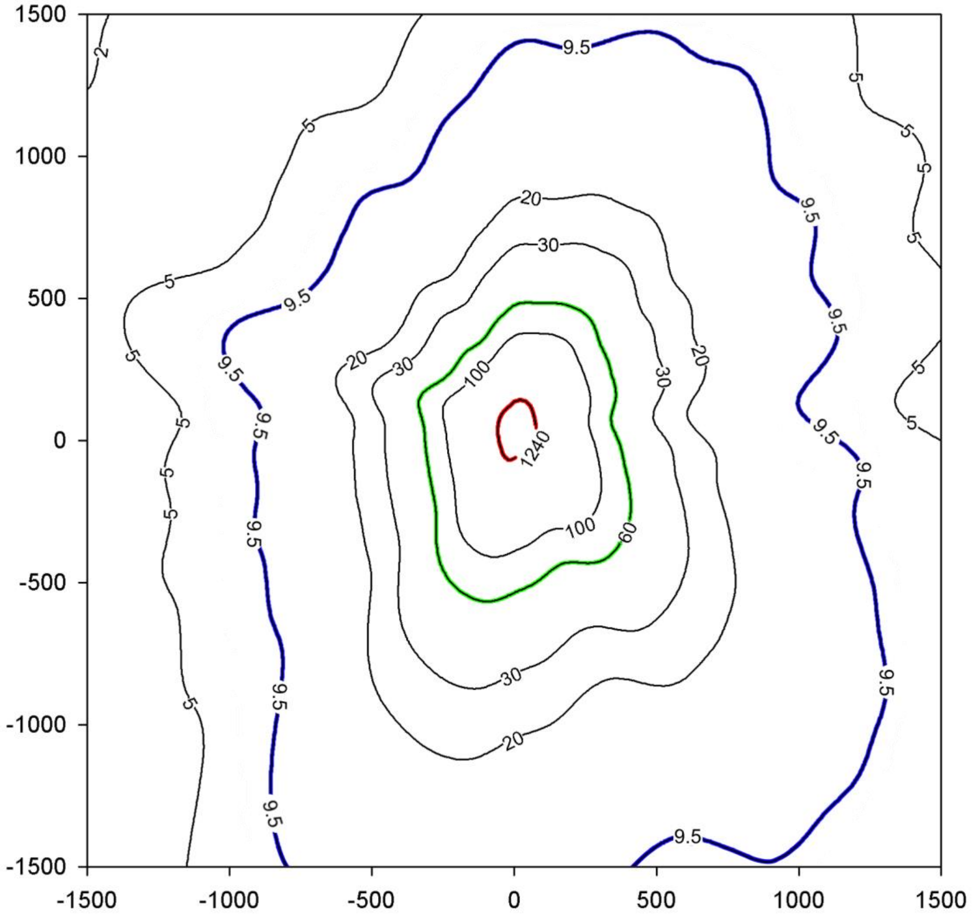

Figure 5.1: Isolines of the PCDD/F deposition (with *TDI 100%* in red, *TDI 5%* in green and *TDI* 10^{-6} in blue) for a biofilter 2 m above the ground; the deposition is expressed in pg I-TEQ m^{-2} y^{-1} and the distance in meters.

With the introduction of the RTO, the land is further protected. A significant impact (*TDI 5%*) is not even observed. A non-optimized zone, where the PCDD/F deposition is higher than *TDI* 10^{-6}, is now limited to a radius of about 250 m. However, the increased costs deriving from the possible adoption of an RTO as an APC solution must be considered. Indeed, in addition to the higher investment costs with respect to biofilters, the economical convenience of RTOs decreases with decreasing concentrations of pollutants, as it will be explained in Section 6.1 with regards to treatment options for VOCs. In the case of VOCs, an interesting alternative to conventional biofilters, based on BTFs, will be presented at Section 5.3. However, given the low solubility of PCDD/Fs, a biological technology would reveal not to be suitable for this purpose and a thermal, catalytic or adsorption treatment would be preferable to achieve satisfying quality targets.

5.2.4 Conclusions

The results of the simulations of PCDD/F deposition showed that a biofilter, whether located at ground level or on the roof of a biostabilisation plant, could not be an appropriate solution in terms of the health risks related to the atmospheric deposition of PCDD/Fs to soil.

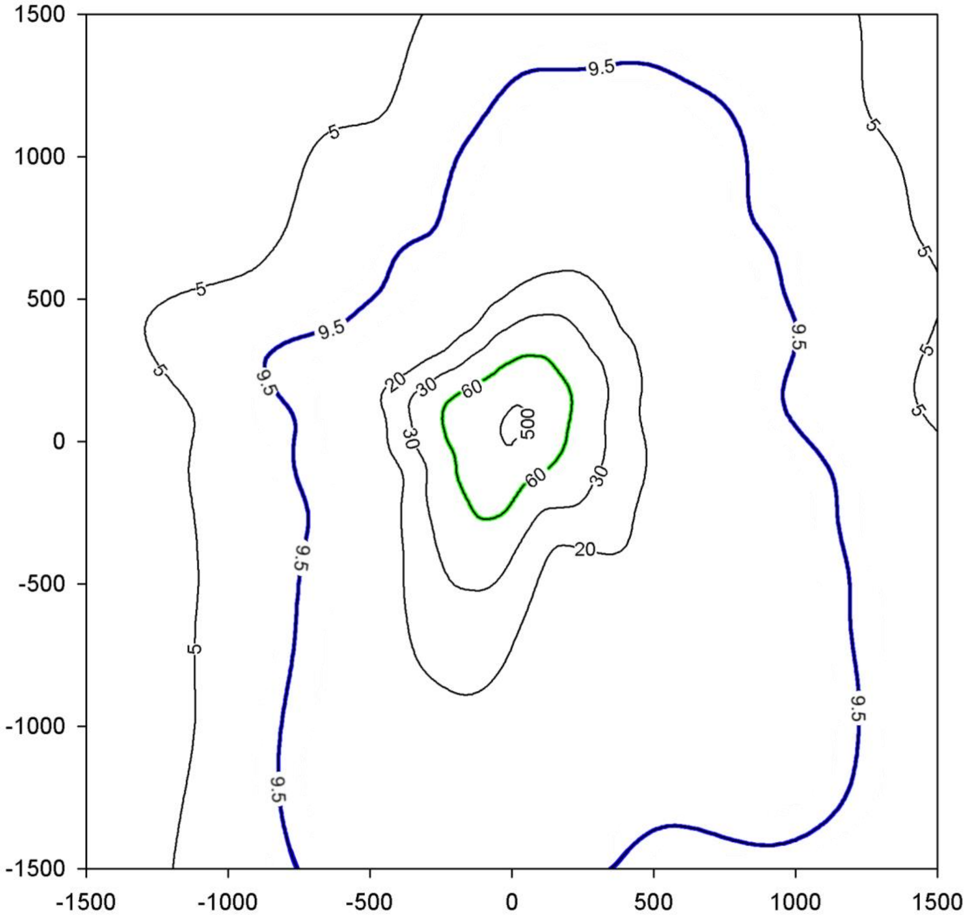

Figure 5.2: Isolines of the PCDD/F deposition (with *TDI 5%* in green and *TDI 10^{-6}* in blue) for a biofilter 17 m above the ground; the deposition is expressed in pg I-TEQ m^{-2} y^{-1} and the distance in meters.

The adoption of the quality parameters proposed here for the quantification and visualization of the expected impacts on health, based on reference PCDD/F deposition values, highlighted the positive role of the RTO technology. A preliminary assessment of the environmental impacts should also be routinely performed for MBTs of MSW, as currently required in the case of incinerators.

The results obtained could help designers to select and optimize exhaust air treatments options. For this purpose, mathematical dispersion models are useful if supported by accurate meteorological data. Hourly meteorological measurements are recommended, for at least one whole year in the area where the plant is planned to be located. The measurements recorded by ground-level meteorological stations may not be enough to characterize a specific area and to adequately simulate the atmospheric dispersion of air pollutants; indeed, nowadays several dispersion models use profilometric data (provided by radio soundings or SODAR) to get a good characterization of the vertical intensity profile and wind direction, as well as the temperature trend.

In order to limit the environmental impact and, above all, the cancer risk for the people living nearby, the farming of those products that have a strong propensity for biomagnification should be regarded with cau-

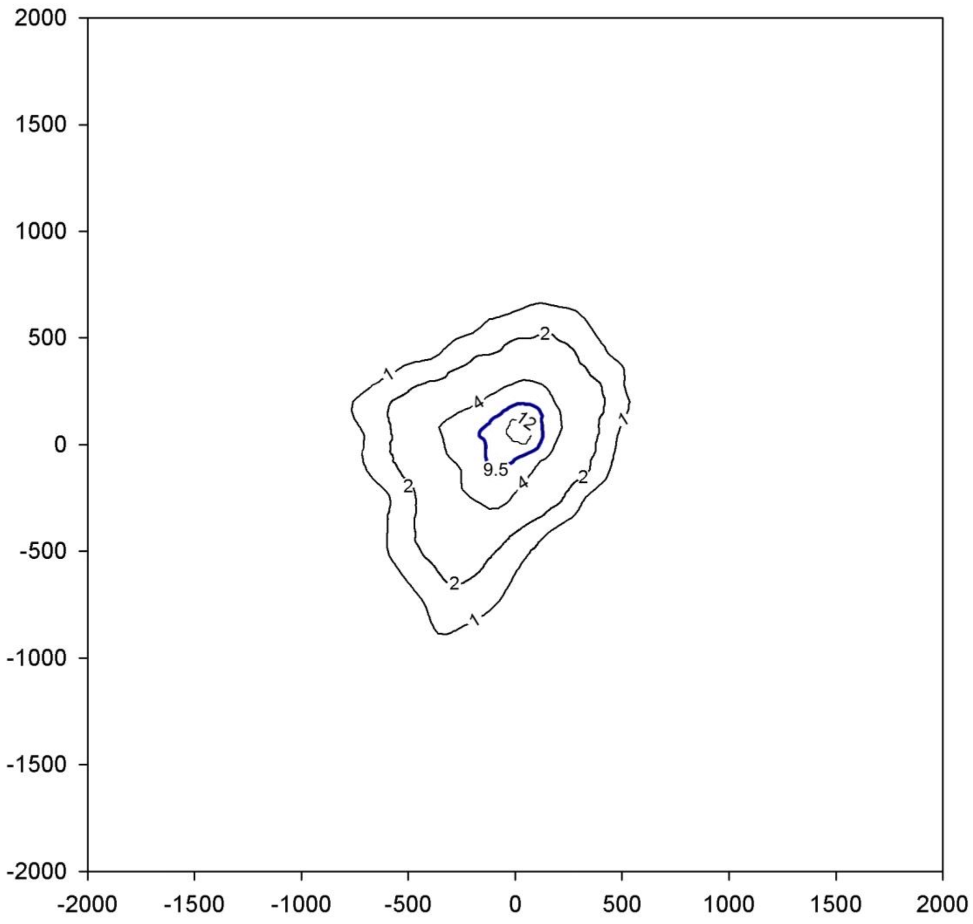

Figure 5.3: Isolines of the PCDD/F deposition (with *TDI* 10^{-6} in blue) for an RTO 25 m above the ground; the deposition is expressed in pg I-TEQ m^{-2} y^{-1} and the distance in meters.

tion, since the consumption of contaminated food can lead to the absorption of PCDD/Fs by the human body. At a source level, conveying emissions and increasing the release height may be an effective solution to improve the dilution of pollutants in the atmosphere.

5.3 Comparison between conventional biofilters and BTFs in terms of atmospheric dispersion

Based on: Schiavon, M., Ragazzi, M., Torretta, V., Rada, E.C., in press. Comparison between conventional biofilters and biotrickling filters applied to waste bio-drying in terms of atmospheric dispersion and air quality. *Environmental Technology*. The final publication is available at Taylor & Francis via http://dx.doi.org/10.1080/09593330.2015.1095246.

5.3.1 Introduction

Air treatment systems based on biological processes have been widely used in treating sulphur compounds, ammonia (NH_3), other odorants and water-soluble VOCs. Biofilters represent the simplest biological air treatment technology. Recent applications of biofilters to remove VOCs from airstreams have been studied both at laboratory (Haque et al., 2012), pilot (Gutiérrez et al., 2014) and industrial scales (Torretta et al., 2015). In the last decade, biofilters have also started to be considered as a promising technology in MBTs of MSW (Clemens and Cuhls, 2003), as a source of VOCs and nuisance, due to their odour impact (Ragazzi et al., 2011).

Their simple configuration makes them a cost-effective solution from the point of view of design and maintenance. However, recent studies have highlighted important drawbacks concerning MBT plants (Vilavert et al., 2014) and the application of conventional open biofilters as an air treatment system (Rada et al., 2011; Almarcha et al., 2012; Copelli et al., 2012). In addition, conventional biofilters have shown low performances compared to other biological technologies, mainly due to the low density of microbes in the filtering medium (Burgess et al., 2001).

Open biofilters cannot guarantee an appropriate dispersion of the outgoing air flow into the atmosphere. A large filtering surface is required to treat medium air flow rates and large areas involve a low speed of the outgoing flow. Biofilters are also generally located at ground level. As a result, the vertical dispersion of the plume is limited, since the dispersion mainly occurs along the horizontal direction. As a consequence, air pollutants and odours may stagnate near the ground. Moreover, due to the high energy consumption needed by the blowers to support ejection from stacks, it is not always feasible to use stacks to convey the flow and improve the dispersion of air contaminants.

New alternative technologies to biofilters have been studied over the last fifteen years: membrane bioreactors have shown a high performance in removing VOCs at low empty bed residence time (*EBRT*), but issues related to the accumulation of excess biomass have been reported, requiring periodical cleaning of the membranes. BTFs are a well consolidated alternative to conventional biofilters. BTFs generally consist of silos whose volume is partially filled with inert packing media (*e.g.*, lava rock, shells, plastic media) that act as a physical support for the growth of microorganisms. A water flow is recirculated over the packing media in order to create a liquid biofilm for the absorption of pollutants, to provide microorganisms with the required amount of nutrients and to carry away excess biomass and microbial decomposition products. Hence, BTFs combine biodegradation with scrubbing.

In comparison with biofilters, BTFs ensure a better control of pH and nutrients, offer a greater stability of operation and lower pressure drops through the filtering media (Álvarez-Hornos et al., 2011; Copelli et al., 2012; Lebrero et al., 2014). Such characteristics have a positive effect on the abatement and on the volume and section area needed, which are considerably reduced with respect to biofilters.

BTFs have gradually entered the market of air treatment technologies and have been commonly adopted as alternative solutions for the abatement of odours, for biogas sweetening, for the removal of VOCs, NH_3 and unwanted substances from industrial activities and WWTPs (Torretta et al., 2013). BTFs are still rarely applied to MBTs, although their application to waste treatment plants has shown good results (Mao et al., 2006; Xue et al., 2013). The effluent treated in a BTF can also be easily conveyed to a discharge pipe, due to the lower volume required by this technology. Conveying the effluent is particularly favourable for the dilution of the outgoing stream, which is not released by an extended surface, as in the case of biofilters. The discharge pipe can also be easily lengthened vertically to improve dilution into the atmosphere.

Considering the potential benefits derived from the adoption of this air treatment technology, the aim of this paper is to analyse possible improvements in the atmospheric dispersion of air pollutants when choosing BTFs instead of a conventional open biofilter, for application to waste MBTs.

This study is part of a research course on the environmental impacts of MBTs in terms of air quality (Rada et al., 2011). Simulations of VOC dispersion in the atmosphere were carried out considering the emissions from a hypothetical MSW biodrying plant. A consolidated model, also used for regulatory purposes, was adopted. Since the MSW facility is a hypothetical plant and no monitoring campaigns are available to perform a calibration of the model, the simulations were run only to obtain approximate indications on the dispersion capacity of the two air treatment technologies.

The simulations concerned two VOCs: dimethyl disulphide (DMDS) and benzene. These VOCs were chosen as reference substances to simulate the impact of biodrying in terms of odours and cancer risk, respectively. DMDS and benzene are normally present in the emissions from MBTs (He et al., 2010; Ragazzi et al., 2011). The relative abundance of DMDS in the waste gas combined with its low odour threshold (Nagata, 2003) makes this substance the most appropriate VOC to simulate the odour impact in the vicinity of a biodrying plant. Likewise, benzene was chosen because of its demonstrated carcinogenicity to humans (IARC, 2015a; US EPA, 2015b). Two different scenarios, concerning the two removal technologies and their configurations, were considered and the results were discussed in order to highlight the dispersion improvements expected by choosing one air treatment technology over the other.

5.3.2 Materials and Methods

5.3.2.1 Size of the hypothetical MSW biodrying plant

The case study refers to a hypothetical medium-sized biodrying plant located in a rural area in the Po Valley (Italy), characterized by a flat terrain. The plant is assumed to treat the residual (unsorted) MSW generated by a population of about 265,000 inhabitants. On the basis of the statistics on a province in the north of Italy, the production of MSW by this reference population is assumed as being equal to 135,700 t_{MSW} y^{-1}. The same reference population contributes to a well-implemented MSW selective collection rate, reaching 65%. The remaining part (35%), equivalent to 47,500 t_{MSW} y^{-1}, is the residual MSW representing the input waste for the hypothetical biodrying plant. Considering the typical value of 10 m^3 of process air per kg of input waste (Rada et al., 2011), the total air flow results in 54,200 m^3 h^{-1}.

5.3.2.2 Definition of scenarios

Average concentrations of DMDS and benzene in the process air were retrieved by a monitoring activity carried out by He et al. (2010) on the biodrying of MSW. These concentrations were scaled on the basis of the composition of the waste of the province taken as a reference for this study, because of the different amount of food waste and, consequently, the different availability of volatile solids. Average concentrations of 10.8 mg Nm^{-3} for DMDS and 4.8 mg Nm^{-3} for benzene were adopted, and the consequent emission factors resulted in 0.163 g s^{-1} and 0.072 g s^{-1} for DMDS and benzene, respectively.

Considerations regarding the air quality were subsequently formulated on the basis of three indicators, one for DMDS and two for benzene. The indicator for DMDS is its odour threshold reported by Nagata (2003), equal to 9.13 µg m^{-3}; therefore, the average concentration of DMDS in the process air corresponds to 1183 OU Nm^{-3}. The first indicator for benzene is its annual mean concentration limit established in the European Union, equal to 5 µg m^{-3} (European Union, 2008). The second indicator for benzene is the ambient air concentration that corresponds to a lifetime excess cancer risk of 1 case in 1,000,000 inhabitants, which is considered the optimal standard value for a risk assessment related to a single compound (US EPA, 1996). This concentration value is calculated by starting from the range of UR_{inhal} recently proposed by the US EPA, between $2.2 \cdot 10^{-6}$ and $7.8 \cdot 10^{-6}$ (US EPA, 2015b). For precautionary reasons, the concentration corresponding to the acceptable cancer risk of 1 case in 1,000,000 was calculated with respect to the lowest value of the range and resulted in 0.13 µg m^{-3}.

Two scenarios were simulated: in the first case, the process air containing VOCs from the MSW biodrying plant is treated by an open biofilter. The volumetric load was assumed as equal to 100 m^3 m^{-2} h^{-1}, compatible with typical biofilter operating conditions for waste air treatment (Kennes et al., 2009). The horizontal area adopted for the biofilter was 550 m^2 and a rectangular configuration (11 m × 50 m) was considered. The height of the biofilter was set to 1 m and a removal efficiency (*RE*) of 80% was assumed, both for DMDS and benzene. This strong approximation was necessary, due to the absence of literature data on the removal efficiencies of both these compounds in complex mixtures emitted by real case studies. The choice of adopting the same *RE* for both DMDS and benzene is also compatible with the purpose of focusing exclusively on the performance of biofilters and BTFs in terms of dispersion of the plume in the atmosphere. Even if assuming different hypothetical removal efficiencies, the results in terms of comparison between the dispersion performance of biofilters and BTFs would not be affected. Accordingly, the concentrations of DMDS and benzene at the exit of the biofilter become 2.16 mg Nm^{-3} (237 OU Nm^{-3}) and 0.96 mg Nm^{-3}, respectively. In the second case, the air cleaning system adopted consists in four identical BTFs acting in parallel, with a diameter and height of 4 m and an EBRT of 12.5 s. The same *RE* of the biofilter (80%) was assumed, both for DMDS and benzene, compatible with the relatively low EBRT of the BTFs adopted here. Similarly to the previous scenario, the absence of literature data forced the adoption of a hypothetical *RE*. The release height of the BTFs was set at 4.5 m above the ground and the velocity of the outgoing stream (in the hypothesis that the air flow temperature is equal to the average ambient air temperature) was 4.7 m s^{-1}, compatible with a diameter of the off-gas pipe of 1 m.

5.3.2.3 Dispersion model

To obtain concentration maps of the VOCs released by a biodrying plant, after application of the two removal technologies considered (biofilter and BTFs), a dispersion model was used. However, in analogy with the previous case (Section 5.2), the primary aim of this study is not to perform a detailed modelling or a model optimization, but to derive indications on the potential impacts expectable by a biodrying plant equipped with two different solutions for VOC control. In addition, the lack of monitoring campaigns on VOCs in the vicinity of the hypothetical biodrying plant does not enable the model to be calibrated. Thus, a consolidated and reliable dispersion model is needed. As in the previous case (Section 5.2), the model chosen was AERMOD, which was taken as a reference for regulatory purposes by the US EPA. AERMOD was recently applied to assess the impact of VOCs on air quality in several studies concerning different emission sources and contexts (Kakosimos et al., 2011; Vilavert et al., 2014; Wang et al., 2014). Other dispersion models, taking into account terrain elevation and obstacles, can be adopted for this purpose. To simulate the impact on air quality and human health, orography and obstacles (*e.g.,* buildings) must be taken into account. However, this does not apply to the study presented here, since the site is located in a flat region.

The meteorological data used in this study are the same adopted in the previous case (Section 5.2). The meteorological data were pre-processed by AERMET. To simulate the dispersion of VOCs related to the two scenarios considered, a square Cartesian grid was adopted. A square domain measuring 4 km × 4 km was chosen and the horizontal resolution was set at 25 m, both in north-south and in east-west directions. Receptors were placed at every node of the grid and located at 1.5 m above the ground, to simulate the impacts on humans. The biofilter was simulated by an areal emission source located in the centre of the calculation domain. The four BTFs were simulated by four point sources located in the centre of the domain, along the north-south direction, and at a distance of 6 m from each other.

5.3.3 Results and discussion

5.3.3.1 Impact of DMDS

The mean annual concentrations of DMDS released by the biodrying with the biofilter and the BTFs are presented in the maps in Figures 1a and 1b, respectively, at 1.5 m above the ground. With the biofilter for the air treatment (Figure 5.4a), DMDS concentrations reached 20 µg m^{-3}, within 25 m from the biofilter, corresponding to 2.19 OU m^{-3}, on the basis of the odour threshold reported by Nagata (2003). The odour threshold of DMDS was not exceeded beyond a radius of about 100 m from the plant. When the BTFs were adopted instead of the open biofilter (Figure 5.4b), the odour threshold of DMDS was never exceeded and the maximal annual mean concentration calculated was 1.5 µg m^{-3}, corresponding to 0.16 OU m^{-3} (Nagata, 2003) achieved in the immediate proximity of the plant.

5.3.3.2 Estimation of the total impact of odorants

To obtain an indication of the total expected impact in terms of odours in the area surrounding the biodrying plant, the following procedure was adopted: the contribution of DMDS to the total odour concentration expected in the exhaust air of a biodrying plant was calculated according to the odour concentrations reported by He et al. (2012). Their work currently represents the most comprehensive study on emissions from MSW biodrying.

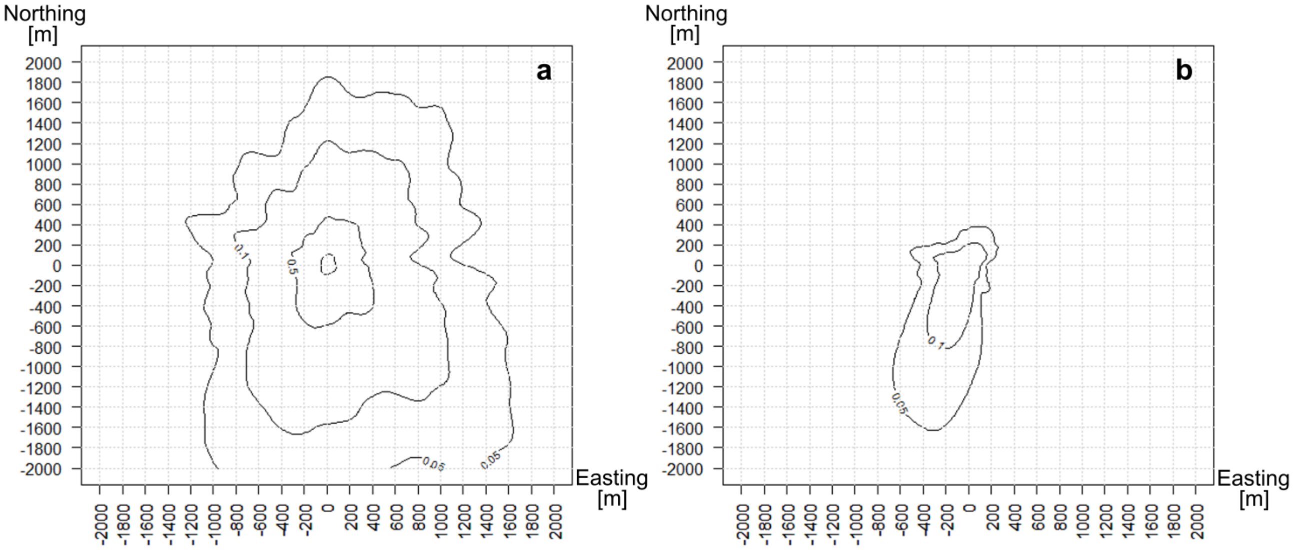

Figure 5.4: Concentration maps of DMDS with *a)* the open biofilter and *b)* the BTFs as air treatment option (distances expressed in meters, concentrations in µg m^{-3}); the dashed line indicates the odour threshold of DMDS.

The calculated ambient DMDS air concentrations were converted to odour concentrations. The maps were re-computed by dividing the DMDS odour concentrations by the contribution of DMDS on the total odour impact, equal to 1.2% (He et al., 2012). The maps reporting the expected total impact in terms of odour were obtained, with the strong assumption that all the main odorants are removed with the same efficiency by the biofilter and by the BTFs. As previously mentioned, such assumption was introduced due to the absence of studies on the removal efficiencies of the compounds listed in He et al. (2012).

In the case of the biofilter (Figure 5.5a), the odour threshold was exceeded within about 650-1000 m in the west-east direction and within 1200-1600 m in the north-south direction. In the vicinity of the biofilter (within a radius of 100-200 m), the odour concentration reached 20 OU m^{-3}, with a maximum of 185 OU m^{-3} within 25 m from the biofilter. This situation significantly improved when adopting BTFs instead of the conventional open biofilter (Figure 5.5b): the odour threshold was exceeded within 200-250 m in the east-west direction and within 200-800 m in the north-south direction, with a maximum of 24 OU m^{-3} within a radius of 25 m from the plant.

Although in these simulations the *RE* was assumed as being equal to that of the biofilter, BTFs convey the treated air and release it at higher levels than conventional biofilters, thus allowing for a better dispersion of the plume. In addition, the velocity of the outgoing flow is higher than that of the biofilters, due to the lower output surface. Therefore, even raising the biofilter to the release height of the BTFs would not provide an adequate solution. By a cell count in the output file of the model, the area characterized by an odour concentration > 1 OU m^{-3} decreased by 91.6% when adopting BTFs instead of a conventional biofilter, changing from 3.46 km^2 to 0.29 km^2.

Starting with the data on odorant concentrations reported in He et al. (2010) and considering the contribution of DMDS compared to the other main odorants reported in He et al. (2012), the total odour concentration estimated in the influent gas was 98575 OU Nm^{-3}, which became 19715 OU Nm^{-3} after the biofilter and

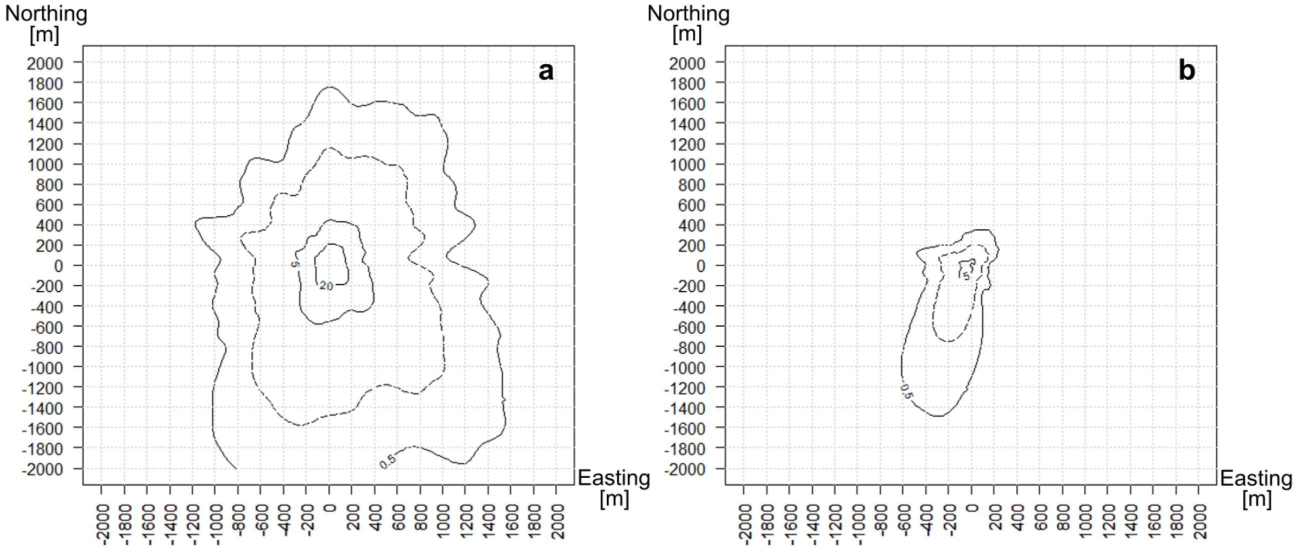

Figure 5.5: Maps reporting the total odour impact expected by the biodrying plant when adopting *a)* the open biofilter and *b)* the BTFs as air treatment option (distances expressed in meters, concentrations in OU m^{-3}); the dashed line refers to the odour concentration of 1 OU m^{-3}.

4929 OU Nm^{-3} after each BTF. In the absence of a national technical regulation on odours in Italy, the guidelines on odour emissions issued by the regional government in Lombardy propose a limit value of 300 OU Nm^{-3} to the emissions from biofilters downstream of MBT plants (Lombardy Region, 2003). To reduce the odour impact on the vicinity of the plant, for any type of land use, biofilters and BTFs might be integrated with additional air treatment options, traditionally scrubbers, or substituted by membrane bioreactors, although more research is needed on the last technology.

However, the odour concentrations at the emissions from the biofilter and the BTFs fall outside of the aim of this study, consisting in a comparison between the impacts expected by these two different air treatment systems in terms of atmospheric dispersion and in the improvements following the adoption of one type of air treatment solution compared to the other. In addition, the results of the simulations in terms of total odour concentrations are just an indication of the impacts expected when choosing one technology instead of the other, due to the strong hypothesis of the identical *RE* for all the odorants considered.

5.3.3.3 Impact of benzene

Similar results to those formulated for DMDS were also found for benzene: the air quality limit value of 5 µg m^{-3} is exceeded within a radius of 50 m around the biofilter. In addition, the area in which the cancer risk induced by benzene is higher than the acceptable value extends up to 900 m from the biofilter (Figure 5.6a). In the case of the BTFs, the air quality limit is respected everywhere and the benzene-induced cancer risk is higher than the acceptable value only within 300 m in the north-south direction and within 150 m in the west-east direction (Figure 5.6b). The area within which the cancer risk is higher than the acceptable value decreased by 95.2%, changing from 1.24 km^2 to 0.06 km^2.

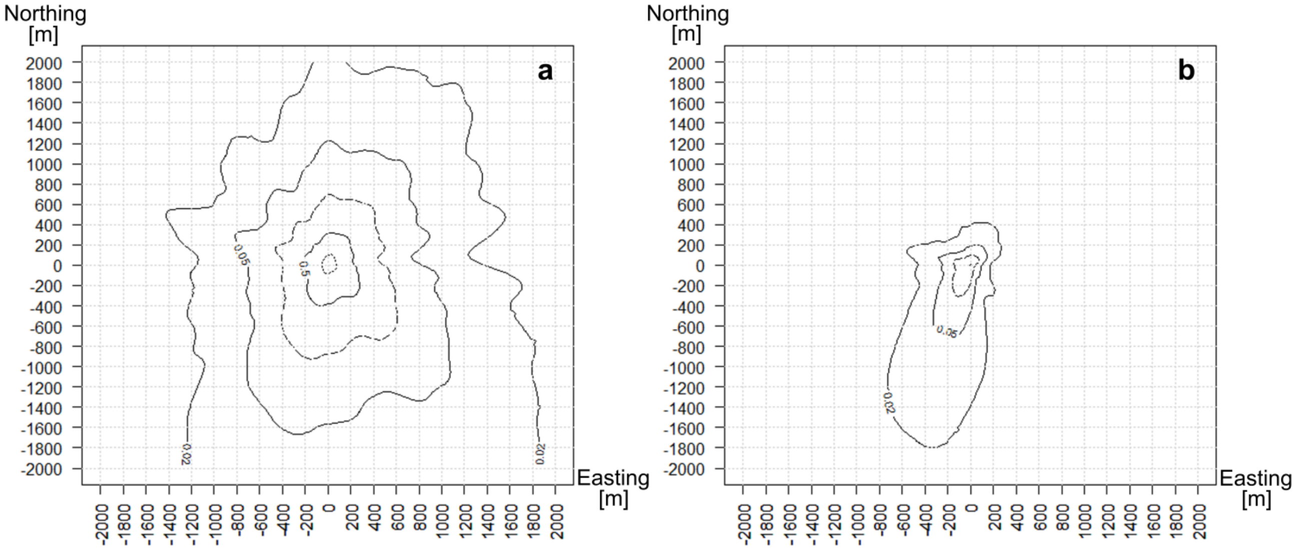

Figure 5.6: Concentration maps of benzene with *a)* the open biofilter and *b)* the BTFs as air treatment option (distances expressed in meters, concentrations in µg m^{-3}); the dashed line indicates the concentration corresponding to the acceptable risk of cancer as a result of exposure to benzene, whilst the dotted line indicates the concentration limit in ambient air.

In order to obtain quantitative indications on the benefits of BTFs over an open biofilter, Figure 5.7 presents the percentages of improvement in the air quality at 1.5 m above the ground between the two scenarios. This map reports the complementary to 1 of the ratio between the concentrations of benzene induced by the BTFs and those induced by the open biofilter. Similar remarks can be made for DMDS. The highest improvements (> 90%) are achieved in the vicinity of the hypothetical MSW biodrying plant, where the concentrations are at their maximum. Lower improvements are obtained at higher distances from the plant as a logical consequence of the higher release height, the higher velocity of the outgoing flow and the consequent fallout of air pollutants far from the plant. However, the concentrations at the border of the calculation domain are not significant.

5.3.4 Conclusions

The dispersion simulations performed by AERMOD highlighted the positive role of BTFs in reducing the impacts on the air quality of the areas located in the vicinity of a hypothetical biodrying plant. The application of BTFs to real cases is expected to lower the mean air concentrations near the ground, thus reducing the odour impact and the cancer risk derived from the exposure of the population to carcinogenic compounds through inhalation. In assuming the same *RE* for the two systems, these positive effects are related to the improved dispersion of air pollutants into the atmosphere. This is because BTFs convey the gaseous effluent and release it at higher levels than open conventional biofilters, which would require significant effort to be retro-fitted with conveying systems. Conveying the effluents means that the most suitable release height can be chosen, which depends on the air quality targets of the area around a plant. In addition, conveying effluents translates into higher velocities of the outgoing air flow, which further improves the dispersion into the atmosphere. More precise indications would be obtained by performing monitoring campaigns near existing

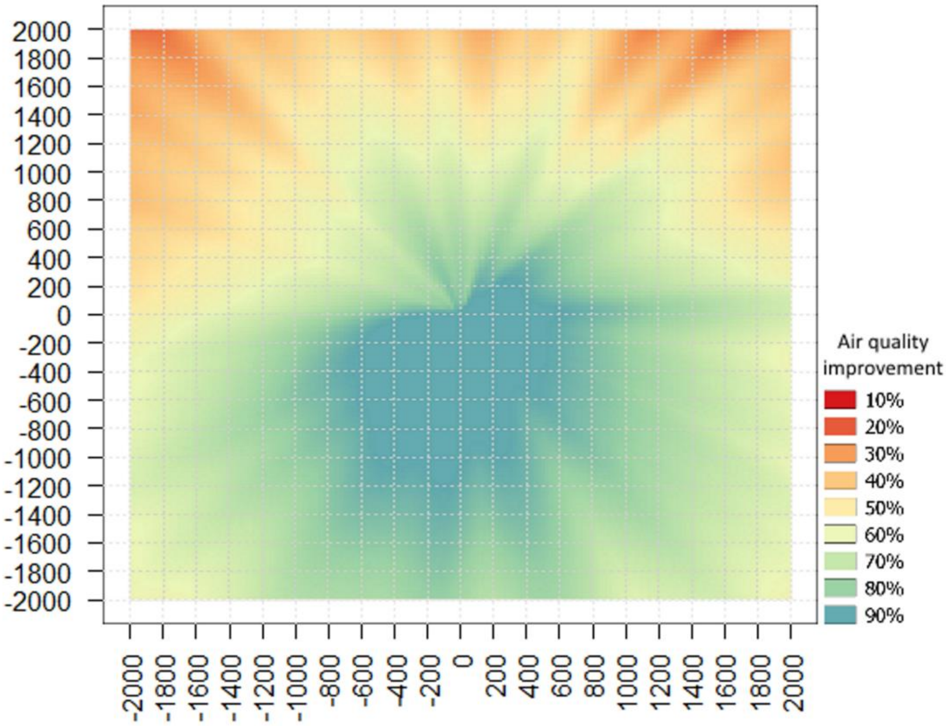

Figure 5.7: Improvements in the air quality at 1.5 m above the ground obtained thanks to the adoption of the four BTFs instead of the open biofilter (distances expressed in meters).

plants and by applying a dispersion model, which would then benefit from a site-specific calibration.

Since the *RE* assumed for BTFs in these simulations was intentionally kept relatively low to highlight the benefits of conveying the flow, real applications may achieve better results in terms of air quality, due to the higher removal efficiencies of BTFs for many air pollutants. Thus, more positive results may be obtained by introducing additional treating systems (*e.g.*, scrubbers) or innovative and cost-effective removal technologies that easily allow conveying the flow (*e.g.*, non-thermal plasma). The optimization of combined systems for air pollution control where biological systems are currently applied is a further step required for this research.

5.4 BTFs: A review on operational aspects and expected performance

Based on: Schiavon, M., Ragazzi, M., Rada, E.C., Torretta, V., in press. Air pollution control through biotrickling filters: A review on operational aspects and expected performance. *Critical Reviews in Biotechnology*. The final publication is available at Taylor & Francis via http://dx.doi.org/10.3109/07388551.2015.1100586.

5.4.1 Introduction

The removal of air pollutants from gaseous effluents has been traditionally achieved through chemical and physical methods, which vary depending on the pollutants to remove. For instance, bag filters, cyclones and electrostatic precipitators are the conventional methods used to remove PM (Vallero, 2014), whilst thermal oxidation, catalytic oxidation, catalytic reduction, adsorption, water or chemical absorption are typical processes employed to remove gaseous pollutants (Doble, 2005; Pourmohammadbagher et al., 2011). When dealing with large flows containing diluted gaseous pollutants (< 100 ppm), the air pollution control becomes economically convenient when adopting methods not involving large amounts of chemicals, adsorbent material, fuel consumption or electric energy, such as biofiltration (Bohn, 1992; Fridman, 2008; Hunter and Oyama, 2000).

The biological removal of pollutants has become attractive for the low investment and operational costs (Bohn, 1992) and the low secondary pollution (Devinny, 1999). Biological methods for the removal of pollutants are based on the biological degradation by bacteria and microorganisms that use the pollutants as substrate for their growth. The purification process is indeed based on the transfer of the undesired compounds from the gaseous phase to an aqueous phase, allowing for the degradation by microorganisms. Usually, the process takes place under aerobic conditions, leading to the transformation of the pollutants into CO_2, water, inorganic compounds and biomass.

In the last few decades, the emission control of VOCs has become a crucial issue owing to their adverse effects to humans, animals, and the environment. Odorous compounds, emitted from a wide variety of sources (wastewater treatment, landfilling and composting, food processing, meat rendering, petrochemical refining, etc.), are not only a direct threat for the human wellbeing, but also contribute to photochemical smog formation and secondary PM (Capelli et al., 2008; Sucker et al., 2008). The main components of the odorous gases are nitrogen-containing compounds, such as NH_3 and nitrous oxide, sulphur-containing compounds, such as hydrogen sulphide (H_2S), terpenes and mercaptans, and VOCs and bioaerosols (Fukumoto et al., 2003; Komilis and Ham, 2006; Akdeniz et al., 2010). NO_x are major constituents of the exhaust gases formed during combustion processes, especially at high temperatures. Ambient NO_x causes serious health and environmental problems such as respiratory diseases and tropospheric O_3 formation (Schiavon et al., 2014a), secondary PM formation , acid rains and acid deposition (Niu et al., 2014).

Traditional methods used to control NO_x emissions, such as selective catalytic and non-catalytic reduction, usually require high temperature and the use of chemicals and catalysts, therefore resulting in high costs; in this framework, biological methods represent a promising alternative (Yang et al., 2012). In addition to being highly toxic and one of the major malodorous compounds emitted from the waste sector and food processing plants (Montebello et al., 2013; Rattanapan et al., 2009), H_2S is corrosive in biogas-fuelled engines. Biological desulfurization processes have proven to be a technically and economically effective alternative to traditional physicochemical processes, especially for low H_2S concentrations (Montebello et al., 2013).

The first biological methods (still widely employed) adopted for air depollution were the conventional biofilters, consisting in one or more beds of a filling material (*e.g.*, peat, compost or a mixture of wood chips, bark and leaves) that provides a high specific surface, high water retention capacity, nutrients and structural support to the biomass (Copelli et al., 2012).

More recently, given the drawbacks of open biofilters discussed in Sections 5.1, 5.2 and 5.3, the research has focused on a variation of biofilters: BTFs, which showed better removal performances with respect to biofilters (Lebrero et al., 2014). In BTFs the volume is filled with inert material supporting the growth of microorganisms. The filling material is continuously humidified by a circulating water flow that allows for the absorption of pollutants and nutrients by the microorganisms and carries away the excess biomass and secondary products. For this reason, BTFs do not require pre-humidification of the air, which reaches saturation rapidly. If compared with conventional biofilters, BTFs ensure greater stability of the process, better pH control, lower pressure drops and lower volume required (Álvarez-Hornos et al., 2011; Copelli et al., 2012; Lebrero et al., 2014), thanks to the continuous trickling of water and nutrients (Mudliar et al., 2010). In recent years, BTFs have been adopted more and more frequently for biogas sweetening and to remove VOCs, NH_3 and odorants from industrial plants and wastewater treatments (Torretta et al., 2013).

Several studies have been recently carried out on BTF applications, providing useful information on their potential in the removal of air pollutants, on the results that can be achieved and on the effects of the different parameters that influence the performances. This paper is intended to investigate the state of the art on BTF applications through the analysis of a group of 16 literature studies chosen as the references for this sector. These 16 studies were selected on the basis of their relevance to the subject and their date of publication, preferring studies carried out during the last decade. The reference studies are analysed and discussed in terms of the operational parameters and of the results obtained, especially with respect to the *RE*s and the elimination capacities (*EC*s) of the pollutants considered.

5.4.2 BTF operation

5.4.2.1 General principles of biodegradation

The microorganisms responsible for biodegradation may be of different nature: fungi, yeasts, moulds and bacteria, usually working under mesophilic conditions. The growth and the metabolic activity of the microorganisms in a biological process depend on the simultaneous compliance with several factors. If the environmental conditions are favourable to the life of microorganisms (*e.g.*, sufficient amounts of nutrients, adequate range of temperature, pH, moisture and O_2 partial pressure), a biological process can develop, leading to consume the pollutants in the contaminated effluents (Delhoménie and Heitz, 2005). However, the conditions that favour the bacterial multiplication vary depending on each species of microorganisms, since each factor can facilitate the reproduction of a species and hinder that of another.

In the aerobic biodegradation, ensuring an adequate supply of nutrients to the microorganism is essential to support their growth. Carbon (C), nitrogen (N) and phosphorus (P) have been demonstrated to ensure good reproduction capability under aerobic conditions when their molar ratio (C:N:P) is 100:10:1 (Maier, 2011).

Temperature affects the reproduction of microorganisms, acting on different metabolic mechanisms and on the bacterial enzymes. Most of the microorganisms used belong to the mesophilic type, having their optimal temperature between 10 and 40 °C (Schnelle and Brown, 2001). Higher temperatures may cause death to the microorganisms, while lower temperatures speed down the metabolic reactions and may inhibit their activity (Schnelle and Brown, 2001; Eifert et al., 2005). Ensuring an adequate range of pH is important for the reproductive process: generally, the optimal pH for heterotrophic species varies between 7 and 8, but lower pH values (1-2) are tolerated (and preferred by specific strains) when removing acids, such as H_2S (Kennes and Veiga, 2001).

Generally, a minimum O_2 content of 5-15% in the inlet gas is required by aerobic heterotrophic microorganisms to survive and oxidize the substrate; specifically, a proper O_2 supply consists in at least 100 parts of O_2 for each part of gaseous substrate (Cabrera et al., 2011).

Moisture is essential, since microorganisms are able to absorb nutrients and substrates only in the aqueous phase (Volkering et al., 1992). The optimum moisture content of the process was evaluated as between 60% and 80% on wet basis (Giri and Pandey, 2013). Lower values may cause drying of the medium and consequent reduction of the biological activity, while excess moisture may promote anaerobic conditions in the medium, due to the occlusion of the voids.

5.4.2.2 Operation principle of BTFs

The operation of BTFs is more complex than that of biofilters, but researches have shown that their operation is more effective, in particular for the treatment of compounds difficult to degrade or for compounds that generate acidic by-products, such as H_2S (Mpanias and Baltzis, 1998). The packing bed of a BTF is located inside a reactor whose walls and geometry must provide structural support to the bed, resistance to corrosion and thermal insulation. For these reasons, real-scale reactors are usually made of glass fibre, polypropylene, polyethylene or polyvinyl chloride (PVC). The biggest difference between BTFs and biofilters is the continuous recirculation of the aqueous phase containing the essential inorganic nutrients. The trickling liquid is circulated back to the top of the filter by a centrifugal pump and is homogenously distributed on the top surface of the bed by nozzles. The circulation water can be passed through a heat exchanger to keep the liquid temperature constant. Nutrients can be fed manually to the circulating liquid or with a micro-pump activated by a process control or by a timer. A schematic representation of a BTF and its components is presented in Figure 5.8.

The pH control can be pursued by addition of caustic soda to the liquid. The contaminated air passes through the packing material, where the pollutants are absorbed to the biofilm that develops around the packing elements. The contaminants absorbed to the biofilm are degraded by the microorganisms and used as an energy source for the bacterial growth. Inert and light materials with medium-high surface areas, such as polyurethane packing media, plastic or ceramic rings and particles, resins, lava rock or shells, are usually adopted as the filtering material, which has the target of favouring the growth of biomass, facilitating the gas and liquid circulation and, meanwhile, avoiding the collapse of the bed (Mudliar et al., 2010; Kennes and Veiga, 2001). Both co-current and counter-current flow configurations are adopted. However, in the case of

VOCs, counter-current operation may cause stripping of the pollutants at the outlet of the BTF (Deshusses and Gabriel, 2005).

Unlike biofilters, where the microorganisms may already be present in the filter, the BTFs should be inoculated, due to the use of inert materials (Bajpai, 2014). The sources typically used for the inoculation of microorganisms are activated sludge derived from WWTPs, samples of soil or water from polluted sites, samples of biomass from other BTFs operating under similar conditions or strains selected and cultivated in laboratory (Deshusses and Gabriel, 2005; Bajpai, 2014). The use of activated sludge as initial microbial inoculum has been previously reported (Oh and Bartha, 1997). The selection of the inoculum becomes increasingly important when the pollutant is more difficult to degrade (Kennes and Veiga, 2001). When carried out, the inoculum selection is normally achieved through the following steps: a sample is taken from one of the aforementioned matrixes containing microorganisms degrading the same or similar pollutants; the sample is diluted in sterilized water; the diluted sample is transferred to a basal medium where the sample is cultured; the sample is transferred to a selective medium, where the pollutants of interests are added as the substrate for the microorganisms; the selected strains are transferred to an enrichment medium, where the microorganisms are further selected; the most high-degrading microorganisms are then identified and inoculated into the packing material of the BTF (Lu et al., 2010). The results of previous researches on the selected microorganisms degrading specific compounds can also be exploited and the most degrading strains can be purchased (Wan et al., 2011).

Like every technology, BTFs have advantages and limitations that can be summarized in Table 5.1. Clogging episodes represent the main drawback of BTF operation (Mudliar et al., 2010). Clogging is caused by the thickening of the biofilm determined by the excessive accumulation of biomass. As a consequence to

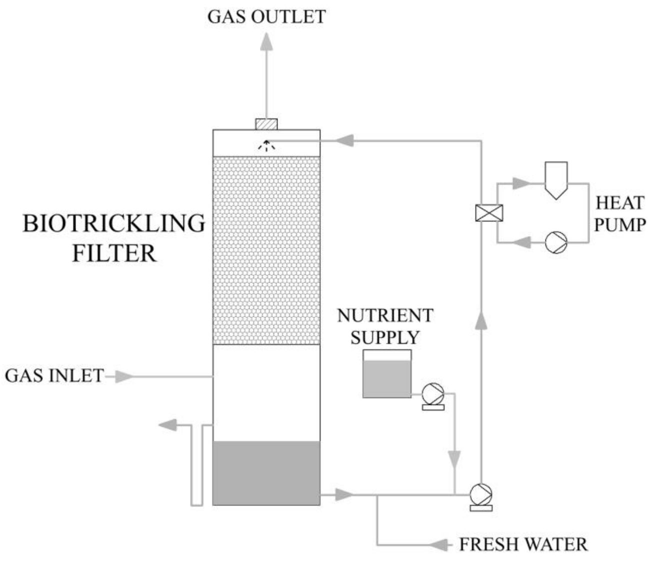

Figure 5.8: General functioning scheme of a BTF.

Table 5.1: Advantages and disadvantages of BTFs.

Advantages	Disadvantages
Lower pressure drop in comparison with biofilters	More complex in operation with respect to biofilters
Medium-low capital and operating costs	Higher probability of clogging
Effective in treating acid degradation products	Production of a waste stream (trickling liquid)
Relatively small footprint required	Higher operating costs with respect to biofilters
pH, temperature and nutrient control	
Limited use of chemicals	

clogging, higher pressure drops, short circuits, the creation of localized anaerobic conditions, the subsequent reduction of the BTF performance and the possible creation of acidic secondary products are possible (Alonso et al., 2000). The control of biomass is the most critical task of BTF operation. Excess biomass growth is generally induced by excessively concentrated streams (> 1000 mg m^{-3}) and consequent high mass loading rates (*ML*s). Also a wrong choice of the packing material may determine clogging problems: gaps of a few millimetres between the elements of the packing material should be guaranteed to avoid excess thickness of the biofilm (Kennes and Veiga, 2002). Also the immobility of the filter bed contributes to clogging: for this reason, mechanical stirring helps releasing the excess biomass through the trickling liquid (Yang et al., 2010). Another option consists in backwashing the filter bed, which gave satisfying results when applied for 1 h once or twice per week (Yang et al., 2010). The addition of chemicals (*e.g.*, sodium or calcium chloride, hydrogen peroxide, caustic soda or sodium hypochlorite) has been proposed as an alternative option for clogging removal (Cox and Deshusses, 1999; Chen and Stewart, 2000), although inhibition of microbial activity occurs (Kennes and Veiga, 2002). Microbial stress induced by reducing the amount of nutrients and water, addition of biomass predators (*e.g.*, protozoa) and starvation are also common strategies to remove clogging (Cox and Deshusses, 1999; Chen and Stewart, 2000; Cai et al., 2004).

5.4.2.3 Influence of the main parameters

The monitoring and maintenance are two very important parts of the process. The parameters routinely monitored in a BTF are the inner temperature, the pH, the dissolved O_2 and the pollutant concentrations at the inlet and at the outlet (Deshusses and Gabriel, 2005), while the typical controlled parameters are the liquid flow rate, the nutrient supply and the dosage of chemicals to re-equilibrate the pH. Additional parameters, important to monitor the phenomenon of clogging and the amount of nutrients in the trickling liquid, are the pressure drop and the liquid conductivity, respectively.

Usual BTF applications take place in the mesophilic field (10-40 °C) (Kennes and Veiga, 2001). In addition to influencing the biological reactions, temperature affects the exchange between the gaseous and liquid phases: an increase in temperature can decrease the Henry’s constant and, at the same time, can increase the diffusion coefficient, facilitating the transfer of mass to the biofilm (Kennes and Veiga, 2001).

The concentration of O_2 in the gas to be treated is typically higher by several orders of magnitude compared to the concentration of the pollutants. In spite of this, its Henry’s constant is relatively high and O_2

may not adequately penetrate into the biofilm and could not be stoichiometrically sufficient to the aerobic biodegradation of the pollutants (Deshusses and Gabriel, 2005). The concentration of O_2 determining O_2 limitation depends on the pollutants to be degraded: the concentration of hydrophilic compounds resulting in O_2 limitation is lower with respect to lipophilic compounds (Deshusses and Gabriel, 2005). Continuous monitoring of dissolved O_2 in the trickling liquid or gaseous O_2 at the outlet of the BTF would give indications on the O_2 available for the biodegradation (Rodriguez et al., 2014).

The optimal pH range depends on the pollutants present in the influent waste gas: the biodegradation of VOCs and NH_3 is performed by heterotrophic microorganisms, whose most suitable conditions are characterized by neutral pH; on the contrary, the biodegradation of H_2S is generally carried out by the *Thiobacillus* strain, whose preferred pH is around 2 (Kennes and Veiga, 2001; Nicolay, 2006).

A fundamental characteristic of BTFs is the recirculation of the liquid phase on the filling bed. The trickling velocity varies greatly, typically from 0.01 to 10 m h^{-1} (Deshusses and Gabriel, 2005). Generally, an increase in the *EC* is observed with the increase of the superficial velocity of the liquid; this is attributed to an increase of the wet surface of the biofilm and to a reduction resistance of the mass transfer in the liquid phase. A balance between the liquid flow rate and the related energy consumption is crucial in view of the optimization of the system in terms of degradation rate and energy costs (Mudliar et al., 2010). In fact, increasing the liquid flow rate results in increasing the surface for the mass transfer between the gaseous and liquid phases (Alonso et al., 2000); on the other hand, higher energy would be requested by the circulation pumps. Furthermore, high trickling rates may increase the resistance to the mass transfer (Deshusses and Gabriel, 2005).

5.4.2.4 Performance parameters

The performance of a BTF can be described by the following main parameters: *RE*, *EC* and *ML* at a specific *EBRT* (Iranpour et al., 2005). *RE* (expressed as percentage) is defined as:

$$RE = \frac{C_{in} - C_{out}}{C_{in}} \qquad \text{Eq. 5.1}$$

where C_{in} and C_{out} are the concentrations of the pollutant at the inlet and at the outlet of the BTF, respectively. *EC* (expressed as g m^{-3} h^{-1}) is the mass of pollutant degraded per unit of time and volume of the filtering bed:

$$EC = \frac{Q_g \left(C_{in} - C_{out}\right)}{V} \qquad \text{Eq. 5.2}$$

where Q_g is the flow rate of the contaminated stream (expressed as m^3 h^{-1}) and V is the volume of the filtering bed (expressed as m^3). *EC* is directly related to the *EBRT*, defined as:

$$EBRT = \frac{V}{Q_g} \qquad \text{Eq. 5.3}$$

which represents the time requested by the influent gaseous stream to pass through the empty volume that the filtering bed would occupy. Typical *EBRT*s vary between 15 and 60 s (Deshusses, 2005), even though cases in which BTFs operate at lower *EBRT*s (2-5 s) have been reported (Deshusses and Gabriel, 2005).

Two additional parameters, useful to understand the effort requested to the BTF in the treatment, are the *ML* and the surface loading rate (*SL*). The *ML*, expressed as g m^{-3} h^{-1}, is defined as the mass of pollutant introduced into the BTF per unit of volume and time (Waweru et al., 2001):

$$ML = \frac{Q_g C_{in}}{V} \qquad \text{Eq. 5.4}$$

A generic representation of the qualitative trends of *RE*, *EC* and *ML*, with respect to the *EBRT*, is presented in Figure 5.9.

Compared to biofilters, whose typical *ML* ranges between 10 and 160 g m^{-3} h^{-1}, BTFs can operate at higher *ML*s, up to 500 g m^{-3} h^{-1} (Iranpour et al., 2005).

SL, expressed as m^3 m^{-2} h^{-1}, represents the volume of air passing through the BTF per unit surface area and per unit time:

$$SL = \frac{Q_g}{A} \qquad \text{Eq. 5.5}$$

where *A* is the area of the BTF cross section. In BTFs, *SL* is typically 100-1000 m^3 m^{-2} h^{-1}, 2 to 5 times higher than biofilters (Iranpour et al., 2005).

5.4.3 Recent researches on BTFs

Hand in hand with the growing interest towards BTFs, an increasing number of studies have been carried out on this technology during the last decade, with the purpose of investigating the effect of the different variables of BTF systems on the performance of the removal of air pollutants. The majority of the studies on BTF applications focus on laboratory- and pilot-scale experiments, although a few larger-scale experiences have been recently carried out (Torretta et al., 2013). In the following sections, a group of recent studies on laboratory- and pilot-scale BTFs for air pollution control are presented and discussed in terms of the configurations and operational parameters chosen and, finally, in terms of the *RE*s and *EC*s achieved. The majority of these studies focus on the removal of VOCs (Liu et al., 2006; Moussavi and Mohseni, 2008; Hassan and Sorial, 2009; Chen et al., 2010; Zhang et al., 2010; Lu et al., 2010; Lebrero et al., 2012; Yang et al., 2013), but also experimental researches on NO (Liang et al., 2012; Yang et al., 2012; Niu et al., 2014), H_2S (Fortuny et al., 2011; Montebello et al., 2013; Chen et al., 2014) and trimethylamine (Wan et al., 2011) are reported.

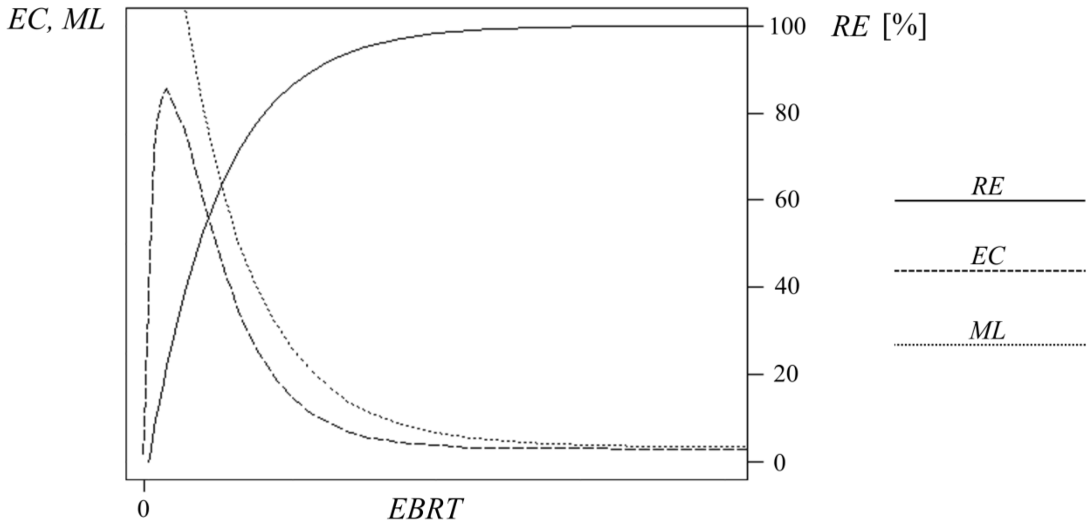

Figure 5.9: Qualitative trends of *RE*, *EC* and *ML* as a function of the *EBRT* in a generic BTF.

5.4.3.1 Presentation of the reference literature studies

Table 5.2 reports the literature studies taken as the reference for this review and the related configurations. The size range of the BTFs studied varies from reactors with an internal diameter of 0.05 m and packing height of 0.30 m (Moussavi and Mohseni, 2008) to an internal diameter of 0.60 m and packing height of 2.00 m (Chen et al., 2014). When mentioned by the authors, the materials used for the construction of the BTFs are glass (Hassan and Sorial, 2009; Chen et al., 2010), Plexiglas® (Liu et al., 2006; Moussavi and Mohseni, 2008; Zhang et al., 2010), PVC (Lebrero et al., 2012, 2014) and polypropylene (Chen et al., 2014). Both cases of single-piece and multi-section BTF columns are reported.

A large variety of packing materials were used in the cited studies: the types employed vary from materials with high porosity, such as polyurethane foam cubes or pellets (Moussavi and Mohseni, 2008; Chen et al., 2010; Lebrero et al., 2012, 2014), porous ceramic beads or particles (Liang et al., 2012; Yang et al., 2012), pelletized diatomaceous earth (Hassan and Sorial, 2009), clays, charcoal or pulverized coal and waste residues (Chen et al., 2014; Lu et al., 2010), to ceramic particles (Liu et al., 2006; Wan et al., 2011; Niu et al., 2014) and more coarse structuring materials, like HD-QPAC®, Pall rings and polypropylene spheres (Zhang et al., 2010; Fortuny et al., 2011; Montebello et al., 2013).

The choice of the inoculum for the treatment may depend on the concentrations of the pollutants in the incoming air or may be related to reasons of time: high concentrations may require the use of specific bacterial strains, which are specialized in the removal of a determined group of pollutants and are able to resist to high pollutant loads; specialized strains can also reduce the start-up phase of the BTF and speed up the achievement of stationary conditions (Veiga and Kennes, 2001; Cox and Deshusses, 2002). The different operational parameters used in the reference literature studies are reported in Table 5.3.

Table 5.2: Description of the experimental setups of the reference literature studies; *D* is the diameter of the BTFs and *H* is the packing height.

Reference	**Type of installation**	***D* [m]**	***H* [m]**	**Pollutant(s) treated**	**Inoculum**	**Filling material**
Chen et al., 2010	1 BTF, made by 3 glass sections	0.12	0.60	Benzene, toluene, *o*-xylene	Mixed communities grown on the influent VOCs	Pelletized polyurethane foam
Qiang et al., 2006	2 BTFs, each made by 6 Plexiglas® sections	0.10	0.60	Xylene	*Bacillus firmus*	Ceramic particles
Lu et al., 2010	1 BTF, undefined material	0.09	1.00	Formaldehyde, benzene, toluene, xylene	*Pseudomonas, Kocuria, Arthrobacter, Bacillus*	Shale, clay, pulverized coal ash, industry waste residues
Zhang et al., 2010	1 BTF, made of Plexiglas®	0.12	1.50	Benzene	n.d.	Polypropylene spheres and fiber balls
Moussavi and Mohseni, 2008	1 BTF, made of Plexiglas®	0.05	0.30	Phenol	Mixed communities from wastewater treatment plant	Polyurethane foam cubes
Lebrero et al., 2012	1 BTF, made of PVC	0.08	1.00	Toluene	n.d.	Polyurethane foam cubes
Hassan and Sorial, 2009	1 BTF, made by 7 glass sections	0.076	0.60	Benzene	n.d.	Pelletized diatomaceous earth
Yang et al., 2013	1 BTF, made of Plexiglas®	0.10	1.10	Chlorobenzene	Mixed communities from wastewater treatment plant	n.d.
Lebrero et al., 2014	1 BTF, made of PVC	0.08	0.53	Methyl-mercaptan, toluene, alpha-pinene and hexane	Mixed communities from wastewater treatment plant	Polyurethane foam cubes
Chen et al., 2014	3 BTFs, made of polypropylene	0.60	2.00	H_2S	Sulfide-oxidizing bacteria from wastewater treatment plant	Bamboo charcoal and ceramsite layers; bamboo charcoal and ceramsite; pure bamboo charcoal
Montebello et al., 2013	1 BTF, undefined material	0.07	0.50	H_2S	Mixed communities from wastewater treatment plant	Stainless steel Pall rings
Fortuny et al., 2011	1 BTF, undefined material	0.07	0.50	H_2S	Mixed communities from wastewater treatment plant	HD-QPAC®
Wan et al., 2011	1 BTF, made of Plexiglas®	0.14	0.60	Trimethylamine	28 species of microorganism (B350 group)	Ceramic particles
Yang et al., 2012	1 BTF, undefined material	0.08	0.30	NO	*Chelatococcus daeguensis* TAD1	Porous ceramic beads and polypropylene-made spheres
Niu et al., 2014	1 BTF, undefined material	0.10	0.19	NO	Mixed communities from wastewater treatment plant	Ceramic beads
Liang et al., 2012	1 BTF, made of Plexiglas®	0.08	0.30	NO	*Chelatococcus daeguensis* TAD1	Porous ceramic particles

Table 5.3: Operational conditions of the reference literature studies.

Reference	Q_g **[m^3 h^{-1}]**	C_{in} **[mg m^{-3}]**	**Total LR [g m^{-3} h^{-1}]**	**Total B_A [m^3 m^{-2} h^{-1}]**	Q_l **[L h^{-1}]**	**Temperature [°C]**	**pH [-]**	**EBRT [s]**
Chen et al., 2010	0.389-1.167	Benzene: 70-550; Toluene: 80-510; *o*-Xylene: 50-510	8.30-154.80	34.40-103.19	10	20-25	7	30-90
Qiang et al., 2006	0.2-1.0	Xylene: 500-3000	21.22-635.64	25.46-127.3	1.5-4.5	n.d.	n.d.	17.0-84.8
Lu et al., 2010	0.6	Formaldehyde: 0-6.5; benzene: 2.2-46.7; toluene: 0.5-28.2; xylene: 4.1-59.0	0.64-13.24	94.31	20	30-40	6-7	40
Zhang et al., 2010	2.8-8.0	Benzene: 45-1050	7.43-495.15	247.57-707.36	5	12-32	6.5-7	15.47-40
Moussavi and Mohseni, 2008	0.036-0.144	Phenol: 829-5180	47-1176	18.33-73.34	6	25	7	15-60
Lebrero et al., 2012	0.36-2.59	Toluene: 5000	360-2571	72-514	4.8	20	n.d.	7-50
Chen et al., 2014	80	H_2S: 4.5-30	0.59-5	282.94	n.d.	20-25	n.d.	25
Hassan and Sorial, 2009	0.082-0.163	Benzene: 258-2750	7.2-76.8	16.31-32.43	0.083	20	7	60-120
Yang et al., 2013	0.35-1.11	Chlorobenzene: 648.90-2019.85	25.96-259.70	44.56-141.33	1.96-6.28	17-28	n.d.	28-90
Lebrero et al., 2014	0.22-2.58	Methyl-mercaptan: 4.9; toluene: 0.82; alpha-pinene: 0.91; hexane: 0.75	0.55-6.64	40-477	8.1	25	7	4-48
Montebello et al., 2013	0.05-0.24	H_2S: 515-3000	52-131	13.7-62.1	14.6	n.d.	2.5-6.5	29-131
Fortuny et al., 2011	0.038-0.23	H_2S: 3000-4500	55-334	10-60	2-77	n.d.	2.5-9.5	30-180
Wan et al., 2011	0.2-0.8	Trimethylamine: 100-600	5.2-26.0	10.83-43.31	7.5 (for 10 min, 16 times a day)	n.d.	n.d.	42-166
Yang et al., 2012	0.036-0.072	NO: 793	19.03-38.06	7.2-14.4	5.4	50	9.3	75-150
Niu et al., 2014	0.09	NO: 123	7.38	11.4	n.d.	24-40	6.8-9.0	60
Liang et al., 2012	0.024-0.181	NO: 133.9-669.6	5.36-64.28	4.5-35.8	12-15	50	7-7.5	30-225

The air flow rate adopted in the reference studies varies greatly: the lowest (0.024 $m^3 h^{-1}$) was used by Liang et al. (2012) as the initial flow rate of their experiments, while a two-order of magnitude higher value (80 $m^3 h^{-1}$) was adopted as the maximal flow rate by Chen et al. (2014). Several studies investigated the effect of the flow rate (or *EBRT*) variation on the performance of the BTFs studied (Liu et al., 2006; Moussavi and Mohseni, 2008; Hassan and Sorial, 2009; Chen et al., 2010; Zhang et al., 2010; Wan et al., 2011; Lebrero et al., 2012, 2014; Montebello et al., 2013; Yang et al., 2013), while the remaining studies focused on the variations of other parameters at a constant flow rate (or *EBRT*). The *EBRT* is usually comprised in the range 15-120 s, although also the effect of extreme values, such as 4 s (Lebrero et al., 2014) and 225 s (Liang et al., 2012), was investigated.

The trickling liquid flow rate showed higher variations, ranging from 0.083 L h^{-1} (Hassan and Sorial, 2009) to 77 L h^{-1} (Fortuny et al., 2011).

The working temperature of a BTF is strictly related to the temperature of the incoming air flow and to the eligible costs, keeping in mind the range of temperature suitable for biodegradation. In the majority of the studies here reported, the temperature is kept around 25 °C, usually with the aid of thermostatic baths. One exception is represented by two studies (Liang et al., 2012; Yang et al., 2012), carried out with a BTF internal temperature of 50 °C. In this case, the need for treating a high-temperature flue gas contaminated by NO_x was fulfilled by the adoption of a specific bacterial strain (the *Chelatococcus daeguensis* TAD1) working under thermophilic conditions (Xu et al., 2014).

The pH of the trickling liquid varies over the reference studies depending on the pollutants treated and on the consequent microorganisms operating the biodegradation. The pH is controlled around neutral values (6-7) in the case of flue gases containing VOCs (Moussavi and Mohseni, 2008; Hassan and Sorial, 2009; Chen et al., 2010; Lu et al., 2010; Zhang et al., 2010; Lebrero et al., 2014) and higher values in the case of NO treatment (Yang et al., 201; Niang et al., 2014); lower values (reaching 2.5) were set for flue gases contaminated by H_2S (Montebello et al., 2013), even though Fortuny et al. (2011) spread the pH range up to 9.5, since a wide pH variation was one of the objects of their study.

5.4.3.2 Results

The start-up phase varies depending on the compounds treated, on the inoculum used (specialized or non-specialized) and on the acclimatization performed. Specialized and adapted bacteria can considerably shorten the start-up phase, which otherwise may last several weeks or about one month (Mathur et al., 2007; Mohammad et al., 2007). Unfortunately, not all the reference studies reported the duration of the start-up phase. Among the remaining studies, interesting results in terms of *RE* and duration of the start-up phase were achieved when using enriched and acclimatized inoculums: Liu et al. (2006) reached a *RE* of xylene of about 80% after 10 d of operation; Montebello et al. (2013) observed a 77% *RE* of H_2S 4 d after the start-up of the system; a higher H_2S *RE* (97%) was obtained only after 2 d of operation by Fortuny et al. (2011); Chen et al. (2010) documented an 87.9% *RE* of benzene, toluene and *o*-xylene (BTo-X) after 4 d of operation; a 99% *RE* of phenol was observed by Moussavi and Mohseni (2008) only 3 d after the start-up of the system; 17 d were required to reach stable conditions and a 100% *RE* of trimethylamine by Wan et al.

(2011); the *RE* of toluene, alpha-pinene and methyl-mercaptan became stable after 4 d in the study performed by Lebrero et al. (2014); *RE*s of nitric oxide above 73% were observed after 15 h by Niu et al. (2014). The following sections report the results achieved during steady-state experiments. The maximal *RE* (RE_{max}) and the corresponding *EBRT* obtained in each study are summarized in Table 5.4. Concerning the studies that report (or allow calculating) the maximal *EC* (EC_{max}), Figure 5.10 reports such results with the respective *ML* and the corresponding *EBRT*. For obvious reasons related to the definition of *EC* (Eq. 5.2) and *ML* (Eq. 5.4), EC_{max} cannot exceed *ML*.

5.4.3.2.1 Biodegradation of VOCs

VOC-contaminated streams are the object of the majority of the reference studies. Chen et al. (2010) focused on the removal of BTo-X in air by gradually increasing the initial concentrations at a fixed *EBRT* of 90 s. An overall *RE* of 94.3% was achieved at a *ML* 25.2 g m^{-3} h^{-1} (Chen et al., 2010). The *EBRT* was subsequently decreased to 60, 45 and 30 s. As a consequence of the increased *ML*, the overall *RE* gradually dropped till about 60%; EC_{max} (97.7 g m^{-3} h^{-1}) was obtained with the lowest *EBRT* considered (Chen et al., 2010).

The same compounds were treated in a BTF at a constant *EBRT* of 40 s (Lu et al., 2010). At the temperature of 30 °C, the *RE* of benzene, toluene and xylene were 65-70%, 93% and 85%, respectively. The respective *RE*s dropped to 48.9-73%, 66.2-75% and 66.3-84% at a temperature of 40 °C, which is farer from the optimum of the *Pseudomonas* (26 °C), the main strain detected in the samples taken from the BTF (Lu et al., 2010).

The chlorobenzene removal was studied by Yang et al. (2013) in relation to the variation of the *EBRT* (from 90 s to 28 s). RE_{max} (97.3%) was achieved at a chlorobenzene initial concentration of 878.53-1522.48 mg m^{-3} and an *EBRT* of 90 s (Yang et al., 2013). EC_{max} (154.32 g m^{-3} h^{-1}) was obtained at an initial concentration of 920.36 - 2019.85 mg m^{-3} and at an *EBRT* of 28 s (Yang et al., 2013).

The limited mass transfer of VOCs from the gaseous phase to the aqueous phase is the object of a study carried out by (Lebrero et al., 2012), which established an optimal ratio between Q_g and the flow rate of the trickling liquid (Q_l) during the treatment of air contaminated with toluene. When adopting polyurethane foam as the packing material, a ratio between 60 and 275 revealed to be optimal and the overall mass transfer coefficient increased linearly with Q_g/Q_l (Lebrero et al., 2012). Higher Q_g to Q_l ratios resulted in lower increases in the overall mass transfer coefficient (Lebrero et al., 2012). In a more recent experiences, Lebrero et al. (2014) compared the performances of a biofilter and a BTF in treating a mixture of air and methyl-mercaptan, toluene, alpha-pinene and hexane by varying the *EBRT* (48, 18, 8 and 4 s). A longer start-up phase (minimum 8 d) was required by the BTF to reach stable *RE*s, probably due to the greater microbial diversity and adsorption to the compost, which was the filling material of the biofilter (Lebrero et al., 2014). High overall *RE*s (> 90%) were obtained in the biofilter at *EBRT*s ≥ 8 s, while an almost-complete overall *RE* was observed in the BTF at *EBRT*s ≥ 4 s (Lebrero et al., 2014). Thus, in spite of a longer start-up phase, the BTF revealed to be more efficient than the compost biofilter at the same conditions.

The phenol removal by a BTF was studied in a recent activity carried out by Moussavi and Mohseni (2008). The initial concentration was varied between 200 and 1000 ppmv and the effect of the *EBRT* (ranging between 15 and 60 s) was investigated. At the highest inlet concentration (1000 ppmv), the *RE* resulted higher than 99% even when decreasing the *EBRT* from 60 s to 30 s, while a decrease in the *EBRT* to 15 s resulted in a RE_{max} of 92% (Moussavi and Mohseni, 2008). EC_{max} (642 g m^{-3} h^{-1}) was obtained by increasing the inlet concentration to 1250 ppmv, at an *EBRT* of 15 s (Moussavi and Mohseni, 2008).

The effects of the initial concentration of benzene and of the carrier height on the removal of benzene was studied by Zhang et al. (2010). The *RE* increased when gradually increasing the initial concentration till a certain value (175 mg m^{-3} at an *EBRT* of about 10 s and Q_l = 5 L h^{-1}), since the microorganisms had not reached their optimal absorption capacity (Zhang et al., 2010). The *RE* was also found proportional to the carrier height. In addition, the pressure drop was found to increase linearly with Q_g (Zhang et al., 2010).

The choice of the packing material affects the *RE* under the same operating conditions. Liu et al. (2006) demonstrated this aspect by assessing the removal of xylene by two identical BTFs filled with two different ceramic materials: spherical particles with porosity of 54% and surface area of 550 m^2 m^{-3} and irregular particles with porosity of 49% and surface area of 680 m^2 m^{-3}. The removal performances were studied by varying the *EBRT* from 84.8 s to 17.0 s (Liu et al., 2006). Similar *RE*s were measured at an *EBRT* between 84.8 and 28.3 s, while irregular ceramic particles showed better performances than spherical particles at an *EBRT* of 17.0 s (Liu et al., 2006). In spite of the better removal performance, the pressure drop related to this type of material was higher; as a consequence, not only the expected *RE*, but also the risk of clogging should be considered when choosing the packing material.

Different biomass control strategies were tested in another study on the removal of benzene in a BTF (Hassan and Sorial, 2009) at different *ML*s (7.2-76.8 g m^{-3} h^{-1}) and different *EBRT*s (60-120 s): 1-h backwashing performed once per week, starvation (no benzene loading for 2 d per week) and stagnation (no flow for 2 d per week). The RE_{max} (> 98%) was obtained at $ML \leq 34.1$ g m^{-3} h^{-1} at steady-state conditions (Hassan and Sorial, 2009). The effect of the different biomass control options was studied at the maximal *ML* (76.8 g m^{-3} h^{-1}): the best performances (*RE* > 80%) were obtained with stagnation, while the worst performances were achieved with starvation; the maximal *EBRT* (120 s) showed always the best results in terms of *RE* (Hassan and Sorial, 2009).

5.4.3.2.2 Biodegradation of H_2S

Three BTFs, equipped with different packing materials (bamboo charcoal and ceramsite layers, bamboo charcoal and ceramsite, pure bamboo charcoal), were studied in a recent study in relation to the removal of H_2S, at an *EBRT* of 25 s and a *ML* of 0.59-5.00 g m^{-3} h^{-1} (Chen et al., 2014). Although all the BTFs showed high *RE*s (> 99%), the BTF equipped with bamboo charcoal and ceramsite layers showed the best results (Chen et al., 2014). Thus, a multi-layer carrier composed of bamboo charcoal and ceramsite reveals to be a cost-effective solution for the removal of H_2S at low *ML*s (Chen et al., 2014).

Pall rings were adopted as the packing material of the BTF studied by Montebello et al. (2013). The removal of H_2S was firstly evaluated by decreasing the *EBRT* from 131 s to 29 s at a constant *ML* of 52 g m^{-3} h^{-1}: *RE* accordingly decreased from 100% to 90%, while EC_{max} (about 50 g m^{-3} h^{-1}) was obtained at an *EBRT* of 76 s (Montebello et al., 2013); in a second stage, the *EBRT* was decreased and the *ML* was stepwise increased from 52 to 301 g m^{-3} h^{-1}, determining a decrease in the *RE* from 100% to 31%, while EC_{max} resulted as 100 g m^{-3} h^{-1} obtained at an *EBRT* of 42 s and a *ML* of 204 g m^{-3} h^{-1} (Montebello et al., 2013). During a period of 160 d, the pH was subsequently decreased from 6-6.5 to 2.5-2.75 at a *ML* of 52 g m^{-3} h^{-1}, but this change did not affect the *RE* of the system, proving its robustness (Montebello et al., 2013).

Fortuny et al. (2011) investigated the performances of a BTF in the removal of H_2S at a constant inlet concentration (2000 ppmv) and decreasing the *EBRT* from 180 s to 30 s (*i.e.,* increasing the *ML* from 56 to 334 g m^{-3} h^{-1}). A *RE* of 97.7% was found to be stable till an *EBRT* of 90 s, while lowering the *EBRT* to 30 s resulted in a *RE* of 39.7% (Fortuny et al., 2011). Almost no reduction in the *RE* was observed when decreasing the *EBRT* from 180 s to 120 s, thus the scale of the system could be reduced with no effects on the H_2S removal. EC_{max} (144 g m^{-3} h^{-1}) was achieved after one year of operation at a *ML* of about 170 g m^{-3} h^{-1} (Fortuny et al., 2011). In addition, Q_l was varied to evaluate the effect of the trickling liquid velocity on the removal. Although no effects were observed on the *RE*, increasing Q_l led to an increase in the availability of O_2 and in the production of sulphate (Fortuny et al., 2011). The BTF also showed high recovery capacity following shutdowns of up to 5 d; in addition, the system was tested in terms of large and sudden pH variations: although no difference was noticed in terms of *RE*, a reduction in the sulphate production was observed when decreasing the pH from neutral conditions to 2.5, probably due to the production of thiosulfate as intermediate, which is subsequently converted to S^0 (Fortuny et al., 2011). The biodegradation was more deeply influenced by increased pH (up to 9.5), since sulphide oxidizing bacteria are generally more tolerant to low pH: in fact, alkaline conditions favour the accumulation of sulphides and polysulphides, which can hinder the activity of sulphide degrading bacteria (Fortuny et al., 2011).

5.4.3.2.3 Biodegradation of nitrogen-based compounds

The effects of the *EBRT* and of the inlet concentrations were evaluated in terms of *RE* and *EC* of trimethylamine (Wan et al., 2011). An *EBRT* higher than 110 s, at an inlet concentration of 300 mg m^{-3}, ensured a 100% removal, while the *RE* decreased to 49.6% when reducing the *EBRT* to 47 s; EC_{max} (13.13 g m^{-3} h^{-1}) was reached at an *EBRT* of 55 s (*ML* = 20.30 g m^{-3} h^{-1}) and the corresponding *RE* was 64.7% (Wan et al., 2011). When varying the inlet concentration (from 120 to 600 mg m^{-3}) at an *EBRT* of 83 s, the *RE* ranged from 100% to 48.4%, while the *EC* varied from 5.04 g m^{-3} h^{-1} (*ML* = 5.04 g m^{-3} h^{-1}) to 12.55 (*ML* = 25.93 g m^{-3} h^{-1}), with a maximum of 14.15 g m^{-3} h^{-1} (*ML* = 18.13 g m^{-3} h^{-1}) at an inlet concentration of 420 mg m^{-3} (Wan et al., 2011). Diffusion and reaction limitations are at the base of the lower *RE*s observed when decreasing the *EBRT* and increasing the inlet concentration. Reaction limitations are responsible for the trend of the *EC*, which firstly increases with the *ML*, due to the enhanced mass transfer, and then slightly decreases, due to the limited contact time for the reactions (Wan et al., 2011).

The removal of NO, at high temperature (50 °C) and after inoculation of *Chelatococcus daeguensis* TAD1, was studied by Yang et al. (2012). A 91.1% *RE* was obtained at an *EBRT* of 150 s and an inlet concentration of 600 ppmv (corresponding to a *ML* of 19.03 g m^{-3} h^{-1}). A lower *RE* (72.2%) was obtained at the same inlet concentration, when decreasing the *EBRT* to 75 s (corresponding to a *ML* of 38.06 g m^{-3} h^{-1}), as a consequence of the limited time available to the microorganisms to degrade NO (Yang et al., 2012). The same group repeated this experience in another research (Liang et al., 2012): the NO inlet concentration fluctuated between 133.9 and 669.6 mg m^{-3}, resulting in an almost constant *RE* comprised between of 86.4% and 89%, at a constant *EBRT* of 90 s (Liang et al., 2012). The *EBRT* was then varied between 30 s and 225 s at a fixed inlet concentration of 535.7 mg m^{-3}. When the *EBRT* is higher than 150 s, *RE*s higher than 90% are obtained and the *RE* slowly increases; conversely, when decreasing the *EBRT*, the *RE* decreases faster, till becoming < 50% at an *EBRT* of 30 s (Liang et al., 2012).

The effect of temperature, pH, chemical oxygen demand (COD) and O_2 concentration were studied by Niu et al. (2014) with respect to the removal of NO, at constant *EBRT* (60 s) and inlet concentration (123 mg m^{-3}). The best conditions, leading to a RE of 99%, were: temperature ≥ 32 °C, pH > 8.0, COD > 165 mg L^{-1} and anaerobic conditions (Niu et al., 2014).

5.4.4 Conclusions

As a result of the survey on the laboratory experiences concerning the application of BTFs, some general conclusions can be derived:

- the *EBRT* is a fundamental parameter influencing both the mass transfer from the air to the biofilm and the biodegradation carried out by the microorganisms, which is characterized by its own kinetics; assuring an adequate *EBRT*, compatible with the contaminant *ML*, is essential not to limit such processes, which are required to obtain high *RE*s; on the other hand, the relationship between *EBRT* and *RE* is linear only at medium-low *RE* values, while the *RE* increases slower with the *EBRT* at high *RE* values; thus, the *EBRT* should be kept as low as possible, close to a satisfying *RE*, in order to obtain a cost-effective scale of the system;

Table 5.4: Values of RE_{max} obtained in the reference studies and respective *ML*s and *EBRT*s.

Reference	RE_{max} [%]	*ML* [g m^{-3} h^{-1}]	*EBRT* [s]	EC_{max} [g m^{-3} h^{-1}]	*ML* [g m^{-3} h^{-1}]	*EBRT* [s]
Chen et al. (2010)	94.3	25.2	90	97.7	146.4	30
Qiang et al. (2006)	100	81.9-178.4	17-84.8	n.d.	n.d.	n.d.
Lu et al. (2010)	65-93	0.64-13.24	40	n.d.	n.d.	n.d.
Zhang et al. (2010)	83	9.79	36	n.d.	n.d.	n.d.
Moussavi and Mohseni (2008)	99	140-564	30	642	1176	15
Lebrero et al. (2012)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chen et al. (2014)	99	0.59-5	25	n.d.	n.d.	n.d.
Hassan and Sorial (2009)	98	34.1	120	60.8	76.8	120
Yang et al. (2013)	97.3	35.14-60.90	90	102.79	154.32-259.70	28
Lebrero et al. (2014)	96.1-99	3.32	8	3.67	6.64	4
Montebello et al. (2013)	100	52	131	100	204	42
Fortuny et al. (2011)	97.7	120	90	144	170	64
Wan et al. (2011)	100	5.20-9.96	83-110	14.15	18.13	83
Yang et al. (2012)	91.1	19.03	150	n.d.	n.d.	n.d.
Niu et al. (2014)	99	7.38	60	n.d.	n.d.	n.d.
Liang et al., 2012)	90	12.86	150	n.d.	n.d.	n.d.

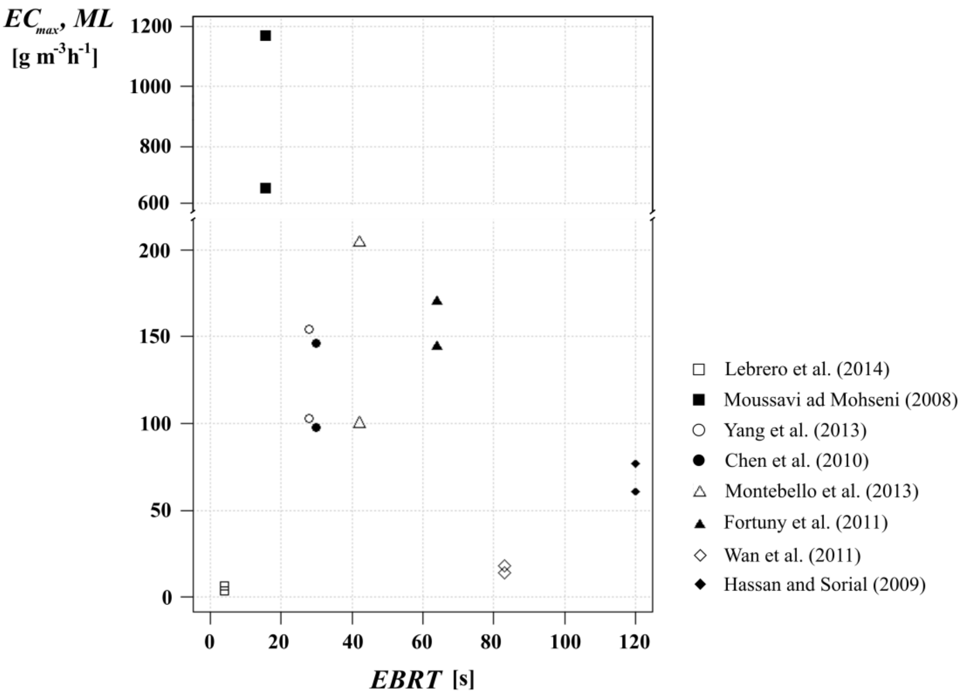

Figure 5.10: EC_{max} obtained in the reference studies and respective *ML*s (upper value of each pair) and *EBRT*.

- to assure an economically feasible operation at larger scales, a compromise between a high *RE* and a high *EC* should be reached; with the exception of cases involving low inlet concentrations of contaminants, EC_{max} is obtained at conditions that differ from those allowing for a high *RE*, since higher *ML*s (and, thus, lower *EBRT*s and higher inlet concentrations) are required;
- the optimal temperature, O_2 concentration in the air flow and pH depend on the pollutants to treat, on the microorganisms involved and on the related reactions of biodegradation; generally, mesophilic conditions are preferred, although thermophilic conditions resulted in good performances in the case of NO_x removal; NO_x showed to be more conveniently removed under anoxic conditions, while O_2 limitation negatively affects the activity of heterotrophic microorganisms; pH showed to be less determinant in the biodegradation performances, even though alkaline conditions may limit the activity of sulphide degrading bacteria;
- controlling the Q_g to Q_l ratio translates into improved mass transfer; an increase in Q_l results in a higher availability of O_2; on the other hand, a slower increase in the mass transfer is observed at high Q_g to Q_l ratios;
- packing media characterized by high surface area are generally capable of offering better performances if compared with other packing materials under the same conditions;
- selecting the inoculum and/or pre-adapting the sample before introducing it into the BTF results in a shorter start-up phase; biomass control strategies based on stagnation are preferred with respect to backwashing or starvation.

6 Proposals for enhanced emission control: Non-thermal plasmas

6.1 Summary

Plasma is defined as an ionized gas, the so-called fourth state of matter, in which the charges of ions and electrons are balanced (Fridman, 2008). Plasmas can be classified according to two main categories: equilibrium and non-equilibrium plasmas. In equilibrium plasmas, electrons, ions and neutral species are in thermal equilibrium and, hence, have the same temperature, which often exceeds 10^4 K (Fridman, 2008). For this reason, equilibrium plasmas are also called "thermal plasmas". On the contrary, in non-equilibrium plasmas, the temperature of electrons can exceed that of heavy particles by 2-3 orders of magnitude; this way, radicals and excited neutral species can be significantly formed while keeping the translational temperature at about 300-400 K (Kim, 2004; Fridman, 2008). This is the reason why non-equilibrium plasmas are usually called "non-thermal plasmas" (NTPs).

During the last decade, considerable research has been carried out on NTPs, due to the fact that they offer the opportunity to destroy or degrade several air pollutants with medium-low amount of energy, depending on the desired *RE*. The majority of studies concern laboratory activities on small-scale reactors and artificial mixtures of air and single VOCs (Orlandini and Riedel, 2004; Magureanu et al., 2007; Huang et al., 2008; Ye et al., 2008; Huang and Ye, 2009; Subrahmanyam et al., 2010; Quoc An et al., 2011; Abdelaziz et al., 2013; Gandhi et al., 2013). These studies demonstrated the effectiveness of NTP in the removal of different VOCs, including the most stable compounds (*e.g.*, aromatics and polyaromatics).

The removal of VOCs has been traditionally achieved through adsorption with activated carbon and incineration, which lose efficiency and become economically disadvantageous in the case of large air flows and low concentrations of pollutants (Copelli et al., 2012). Other treatment systems, such as biological treatments, are known for their low energy consumption and are frequently applied to MBTs. On the other hand, as anticipated in Chapter 5, both biofilters and BTFs are susceptible to flow rate variations, require time to adapt to the new conditions and may be inefficient during non-steady state periods. On the contrary, NTP systems can be adapted to a wide range of flow rates by acting on the main variables governing the system (*e.g.*, frequency and voltage applied and the amount of energy transferred by the duty cycle chosen).

NTPs can be generated by different types of discharge: corona discharge, dielectric barrier discharge (DBD) and electron beam irradiation. Among these, DBD is the most widely investigated type, since DBD reactors allow for stable and reproducible plasma conditions (Preis et al., 2013). Two geometrical configurations can be adopted: cylindrical or planar. Both of them include a high-voltage electrode, separated from the ground electrode by a gap containing a discharge volume and at least one dielectric (Kim, 2004). Thanks to the dielectric barrier, the transfer of charge through a single discharge and the formation of a spark are prevented, since the charge is transferred through a multitude of micro-discharges in the gap (Fridman et al., 2005; Vandenbroucke et al., 2011). Due to the presence of a dielectric barrier, the reactor cannot operate with direct current but requires alternate power supply.

The chemistry of NTPs starts with the electrons excited by the energy of the electric field. Given the lower mass of electrons, compared to ions and neutrals, they gain much more energy than the other species. Molecules in the gaseous streams are then activated by collisions with the high-energy electrons, producing ionization and dissociation. In air plasmas, the presence of oxygen and humidity leads to the production of O_3, ·OH and peroxy radicals. The destruction of VOCs in air is ascribed to their oxidation by the species generated in plasma. In the case of mixtures of air and VOCs, the oxidation mechanism of hydrocarbons depends on the molecular structure of each compound: aromatic hydrocarbons are subject to the transfer of a positive ion charge and to subsequent oxidation operated by the radicals present in plasma; saturated hydrocarbons undergo dehydrogenization, subsequent oxidation of the resulting radicals to form peroxy radicals and, finally, either total oxidation to CO_2 and H_2O or activation of a chain of reactions with hydroperoxyde radicals; unsaturated hydrocarbons are subject to the same oxidation mechanisms of saturated compounds, with a further final radical addition (PlasTEP, 2014).

Pilot-scale experiences of DBD applications show encouraging results in the removal of VOCs, although only a few tests have been reported in the literature (Mizuno, 2007; Ye et al., 2008). Possible limitations may concern the energy required to treat large flow rates. In this case, the combination of NTP with other removal technologies represents an interesting matter of investigation. This considered, this chapter presents two experimental studies, concerning the treatment of VOCs with DBDs and the possible interactions with biological depollution systems. Both these studies are the object of two papers written during this doctoral research, with the purpose of proposing an enhanced method for the decontamination of VOC-polluted streams and, thus, limiting human exposure by acting on the side of prevention at the emission level. These two experimental activities move from the preliminary results obtained in a previous research on the application of a DBD to a mixture of synthetic air and methyl ethyl ketone (Ragazzi et al., 2014c), a typical component of the effluents from MBTs of waste.

6.2 Potential of NTPs for helping the biodegradation of VOCs

Based on: Schiavon, M., Scapinello, M., Tosi, P., Ragazzi, M., Torretta, V., Rada, E.C., 2015. Potential of non-thermal plasmas for helping the biodegradation of volatile organic compounds (VOCs) released by waste management plants. *Journal of Cleaner Production* 104, 211-219. The final publication is available at Elsevier via http://dx.doi.org/ 10.1016/j.jclepro.2015.05.034.

6.2.1 Introduction

At a European level, VOC emissions have decreased for the last twenty years, especially due to increasingly stringent emission limits in the transportation sector. However, the waste sector still contributes up to 4% of VOC emissions (European Environment Agency, 2012). Within this sector, MBTs have been growing in popularity in the last twenty years, because of their important role in integrated systems for waste management and because of the increasing awareness that waste represents a resource, especially in terms of energy (Urbaniec and Bakker, 2015). Along with other compounds (*e.g.*, NH_3, CO_2, CO, methane, PCDD/Fs and PCBs), MBT plants release a large variety of VOCs, whose composition mainly depends on the quality of the input waste (Prenafeta-Boldú et al., 2012; Dorado et al., 2014). As highlighted in Chapter 5, conventional biofilters, traditionally adopted as removal technologies for waste-gas treatment, shows poor performances in terms of dispersion of the plume into the atmosphere, due to the relatively low temperature of the outgoing flow, the low emission velocity and the low release height, since biofilters are generally located at ground level (Rada et al., 2011). Such drawbacks were pointed out a decade ago, suggesting the adoption of closed biofilters, incorporating a stack in order to convey the waste gas and improve the dispersion within the atmosphere (Rada et al., 2005). Unfortunately, this approach cannot be always adopted as the costs of energy for the blowers supporting the aspiration could be very high. As presented in Chapter 5, an improvement with respect to biofilters is represented by BTFs. However, biodegradation is particularly sensitive to changes in the composition of the gaseous effluent and to unsteady air flow rates (Almarcha et al., 2012; Torretta et al., 2013), since microorganisms require time to acclimatize to the new conditions (Elías et al., 2010). During transient conditions, the *RE* of biological technologies may be inadequate. Consequently, an upstream device that integrate the gas treatment in order to improve the performance of a biofilter would be well received by the customers and its adjustable characteristics would optimize the energy costs.

In this framework, atmospheric NTPs may become a promising technique for removing several air pollutants (Thevenet et al., 2014; Stasiulaitiene et al., 2015), because the energy of the electric field is largely transferred to electrons; as a consequence, electron dissociation processes promote a “high energy” chemistry (plasma chemistry), which fosters excitation and molecular dissociation also in very stable molecules. Several studies on laboratory applications of the DBD for VOC removal focused on single VOCs, whilst real emissions from industrial or waste treatment plants include a large variety of compounds. However, the number of studies focusing on mixtures of VOCs is still limited. Thus, the aim of this research is to investigate the effect of NTPs applied to mixtures of VOCs representing real emissions from specific industrial and waste treatment processes that use biofiltration or biotrickling filtration for APC. Given that NTPs are still not commonly applied as an air treatment option in the industrial sector, this study shows a potential application of this process (already investigated in details in applied physics) in the field of environmental engineering.

This study focuses on the DBD treatment of two VOC mixtures: one containing compounds typically present in industrial printing houses (ethanol and ethyl acetate) and the other containing VOCs that are characteristic constituents of the gaseous effluents of wastewater treatments in petrochemical plants (benzene, toluene and octane). Since all these compounds are also present in the MBTs of municipal solid waste (Umwelt Bundesamt, 1998), the application of an NTP also provides useful information on the opportunities offered by such treatments in MBT plants. In particular, this section presents results on VOC remediation that may help to understand the feasibility of exploiting NTPs in the waste sector and their ability to overcome the typical issues of biofiltration for APC. Particular importance is given to the identification of the byproducts formed during the NTP treatment, since substances even more hazardous than the initial compounds may be formed. Insights into the possible configurations of air-cleaning systems that include NTP are also presented.

6.2.2 Material and Methods

6.2.2.1 Experimental setup

The experimental apparatus consists in a VOC generator, a DBD reactor, the hydraulic circuit and the electric circuit (Figure 6.1). Details of the experimental setup are presented in Figure 6.2. The VOC generator is composed of two bubblers: one contains the mixture of organic solvents, precursors of the organic vapours; the other one contains deionized water and humidifies the flow. The flow consists of dry synthetic air containing 80% nitrogen and 20% oxygen (Air Liquide S.A.). The air flow is split into three lines: one passing through the bubbler containing VOCs, one through the bubbler containing water and one used as a carrier for the VOC/water mixture. The three air flows are regulated by three mass flow controllers (M1, M2, and M3, respectively). The bubblers are placed in a thermostatic bath and kept at a constant temperature of 23 ± 1 °C. By regulating the flows and the temperature, the composition of the mixture in vapour phase in equilibrium with the liquid phase can be obtained by the Raoult’s law and Antoine’s relation. The three flows are mixed together. The resulting flow is measured by an additional controller (M4) placed upstream of the DBD reactor. The hydraulic circuit of the system is made up of Teflon tubes and metallic pipelines.

The DBD reactor consists of a quartz tube (inner diameter of 10 mm and outer diameter of 13 mm) where a copper ground electrode (outer diameter of 8 mm) is inserted. There is a 1-mm gap between the electrode and the dielectric. A silver paste, coating the quartz tube for a length of 170 mm, acts as the high-voltage electrode. The high-voltage generator is composed of a wave-form generator (WFG-Agilent 33220A, Agilent Technologies Inc.) that provides the sinusoidal excitation, a power amplifier (AMP-Hypex UCD2k OEM, Hypex Electronics B.V.) and a high-voltage transformer (VHT-Amp-Line Al-T1000.7-P100, VHT Amplification). A frequency of 4 kHz and a peak voltage of 15 kV were chosen. The discharge current is

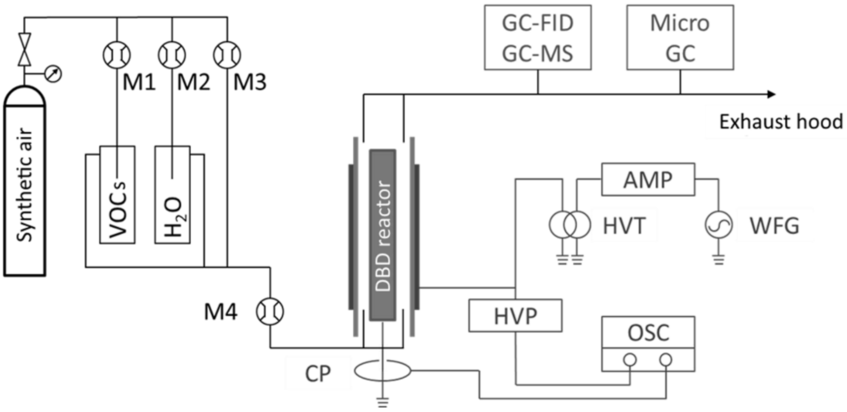

Figure 6.1: Configuration of the experimental setup (HVP: High-Voltage Probe; OSC: Oscilloscope; HVT: High-Voltage Transformer; AMP: Amplifier; WFG: Wave Form Generator).

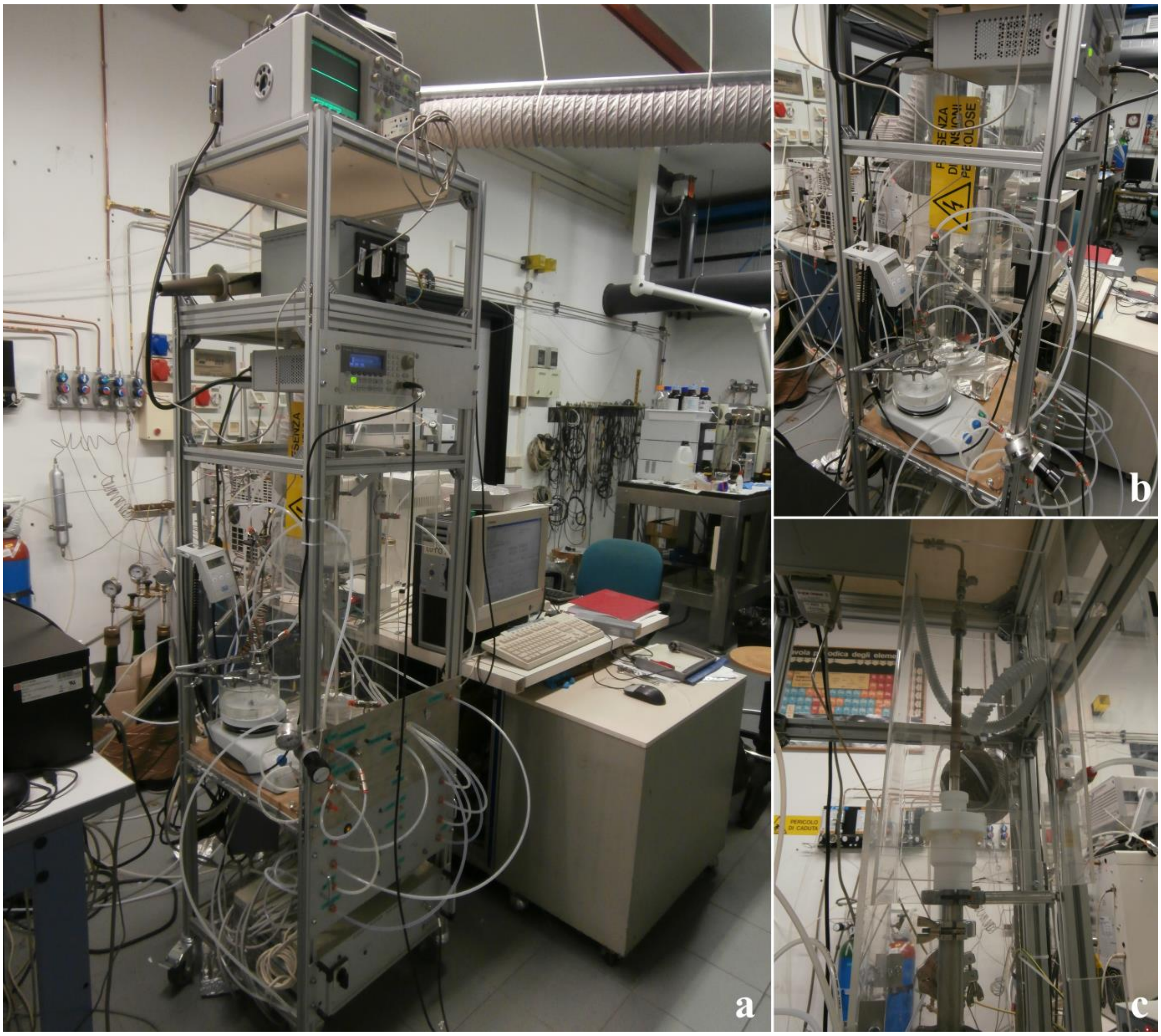

Figure 6.2: *a)* Overview of the overall experimental setup, *b)* detail of the bubblers and *c)* of the DBD reactor.

measured by a Magnelab CT-01-b probe (Farnell UK Ltd.), and the voltage by a HVP Tektronix P6015A high-voltage probe (Farnell UK Ltd.). During each measurement session, both current and voltage signals were recorded by an OSC-Agilent 54642D oscilloscope (Agilent Technologies Inc.), and processed to obtain the power transferred to the system by the integration of their product, according to the Lissajous figure method. The accuracy of the power values was calculated as being 8%.

6.2.2.2 VOC mixtures

The first VOC mixture (Mixture 1) is composed of ethanol and ethyl acetate. Mixture 1 represents typical effluents of the printing industry, containing the solvent removed from the plastic film on which the ink is applied. Table 6.1 reports the concentrations of ethanol and ethyl acetate adopted in this study, which derive from field data concerning the emissions from a printing house. To understand the dependence of the removal by NTP on the initial concentrations of VOCs, three treatment sessions were carried out with three different sets of concentrations of ethanol and ethyl acetate, while keeping their volume ratio constant. The concentrations were adjusted by regulating the flow controller M1.

BTFs have been widely applied in VOC removal and odour treatments (Sempere et al., 2012). The complete biodegradation of ethyl acetate in BTFs is poor, leading to the formation of ethanol as intermediate product (Deshusses et al., 1999). Unlike ethyl acetate, ethanol is completely miscible in water. Therefore, pre-treating ethyl acetate with an NTP system may facilitate the bacteria to remove the solvents in the biological reactor.

The second mixture (Mixture 2) is composed of benzene, toluene and octane. These compounds were selected in order to investigate the performances of NTP in the removal of VOCs present in the humid air coming from the treatment of liquid effluents released by petrochemical plants. Octane was chosen as an example of aliphatic hydrocarbon, toluene as an aromatic hydrocarbon, and benzene as a harmful pollutant and carcinogenic compound. Biotechnological methods such as bioscrubbers, BTFs and conventional biofilters, have been usually employed for their removal (Delhomenie et al., 2002; Yuwono and Lammers, 2004) and are listed as the BATs for the control of odour and VOC emissions from oil refining (European Commission, 2015) and petrochemical processes (European Commission, 2003). Bioscrubbers can be adopted as a pre-treatment stage upstream of BTFs. However, bioscrubbers require a high consumption of water even when operating only as a pre-treatment system, thus with no need to ensure high removal efficiencies. An NTP treatment may be a suitable solution to replace this first stage.

Four different initial VOC concentrations were chosen (Table 6.2), measured at different stages of the air pollution control system of an existing industrial WWTP. The treatments of the mixtures with high VOC concentrations (Mixture 2.1 and Mixture 2.2) may indicate whether a bioscrubber could be replaced with an NTP, and the performance of NTP on the mixtures with low VOC concentrations (Mixture 2.3 and Mixture 2.4) may suggest replacing the BTF stage with an NTP system.

6.2.2.3 Analytical instrumentation

The analyses of the gaseous effluents were carried out online by means of chromatographic techniques. An Agilent 3000 Micro GC Gas Analyzer (Agilent Technologies Inc.) was used to measure CO and CO_2. CO was measured by an HP-PLOT MoleSieve capillary column and CO_2 by a PLOT U capillary column (Ag-

Table 6.1: Average initial concentrations and corresponding *ML*s of the three mixtures of ethanol and ethyl acetate.

	Ethanol		**Ethyl Acetate**	
	Concentration [ppm]	***ML*** **[g m^{-3} h^{-1}]**	**Concentration [ppm]**	***ML*** **[g m^{-3} h^{-1}]**
Mixture 1.1	604 ± 40	4205 ± 326	778 ± 40	10360 ± 650
Mixture 1.2	346 ± 21	2409 ± 174	358 ± 18	4767 ± 294
Mixture 1.3	233 ± 14	1622 ± 116	216 ± 11	2876 ± 179

Table 6.2: Average initial concentrations and corresponding *ML*s of the four mixtures of benzene, toluene and octane.

	Benzene		Toluene		Octane	
	Concentration [ppm]	***ML*** **[g m^{-3} h^{-1}]**	**Concentration [ppm]**	***ML*** **[g m^{-3} h^{-1}]**	**Concentration [ppm]**	***ML*** **[g m^{-3} h^{-1}]**
Mixture 2.1	72 ± 4	850 ± 57	344 ± 21	4790 ± 347	352 ± 21	6077 ± 432
Mixture 2.2	25.0 ± 1.5	295 ± 21	164 ± 10	2284 ± 165	183 ± 11	3159 ± 226
Mixture 2.3	11.0 ± 0.7	130 ± 10	87 ± 5	1211 ± 83	107 ± 6	1847 ± 125
Mixture 2.4	6.0 ± 0.4	71 ± 6	53 ± 3	738 ± 50	65 ± 4	1122 ± 82

ilent Technologies Inc.). A thermal conductivity detector (TCD) was used to detect these two compounds.

A Finnigan Trace GC Ultra (Thermo Fisher Scientific Inc.), equipped with a flame ionization detector (FID) and an MS, was used to identify and quantify the VOCs in the mixtures and the byproducts. Injection reproducibility was guaranteed by an automatic six-port valve system with a loop of 1 mL. HP-PLOT Q capillary columns (Agilent Technologies Inc.) were used to analyse Mixture 1, whilst Mixture 2 was analysed by DB-5 capillary columns (Agilent Technologies Inc.).

The concentrations were obtained by using an external calibration. The reproducibility of Micro GC and GC-FID/MS was evaluated as 2% and 5%, respectively.

6.2.2.4 Measurement procedure

Each different mixture was treated in the DBD reactor by varying the energy supplied to the discharge: all the measurements were performed at a frequency of 4 kHz, but the energy transferred to the system was modulated by changing the duty cycle (*i.e.*, the fraction of time during which the discharge is active). The peak-voltage applied was kept at 15 kV, except for the sessions at lower energy, during which the voltage was reduced to 11.8 kV. The relative humidity (*RH*) of the carrier flow was kept stable at 33% and the total flow rate entering the DBD was 0.005 L s^{-1}, with a residence time of 0.98 s in the reactor.

The *RE* of the initial compounds was calculated according to Eq. 5.1, at a given specific energy density (*SED*). Although the purpose of the present research is not to compare NTP and biofiltration, but to assess the potential benefits deriving from a combination of the two technologies, *ML* (Eq. 5.4) and *EC* (Eq. 5.2) were also calculated to facilitate a comparison with biofiltration systems in future research. In these calculations, the volume of the reactor was considered as equal to the discharge volume (49 mL). The *SED*, expressed in terms of J L^{-1}, is defined as:

$$SED = \frac{P}{Q_g} \qquad \text{Eq. 6.1}$$

where P is the discharge power and Q_g is expressed as m^3 h^{-1}.

To assess the performance of the NTP treatment on the removal of the initial compounds, the selectivity to CO_2 (SCO_2) was calculated for Mixture 1 (Eq. 6.2) and Mixture 2 (Eq. 6.3):

$$SCO_2 = \frac{[CO_2]}{2([C_2H_6O]_0 - [C_2H_6O]) + 4([C_4H_8O_2] \; - [C_4H_8O_2])} \tag{Eq. 6.2}$$

$$SCO_2 = \frac{[CO_2]}{6([C_6H_6]_0 - [C_6H_6]) + 7([C_7H_8]_0 - [C_7H_8]) + 8([C_8H_{18}]_0 - [C_8H_{18}])} \tag{Eq. 6.3}$$

where $[CO_2]$, $[C_2H_6O]$, $[C_4H_8O_2]$, $[C_6H_6]$, $[C_7H_8]$ and $[C_8H_{18}]$ are the CO_2, ethanol, ethyl acetate, benzene, toluene and octane concentrations at a specific *SED*, respectively. Initial VOC concentrations are marked with the “0” subscript. The coefficients at the denominators refer to the number of carbon atoms provided by the initial compounds with respect to CO_2, according to the following reactions of total oxidation for Mixture 1 (Eq. 6.4) and Mixture 2 (Eq. 6.5):

$$xC_4H_8O_2 + yC_2H_6O + (5x + 3y)O_2 \longrightarrow (4x + 2y)CO_2 + (4x + 3y)H_2O \tag{Eq. 6.4}$$

$$xC_6H_6 + yC_7H_8 + zC_8H_{18} + \left(\frac{15}{2}x + 9y + \frac{25}{2}z\right)O_2 \longrightarrow (6x + 7y + 8z)CO_2 + (3x + 4y + 9z)H_2O \tag{Eq. 6.5}$$

Useful information for scaling the system up can be provided by calculating the energy yield (*Ey*) for each VOC at a given *SED*, defined as:

$$Ey = \frac{C_{in} - C_{out}}{SED} \tag{Eq. 6.6}$$

The errors associated with *ML*, *RE*, *EC*, *SED*, SCO_2 and *Ey* were calculated by the error propagation formula.

6.2.3 Results and discussion

6.2.3.1 Removal efficiencies and elimination capacities

The *RE*s of ethanol and ethyl acetate are presented in Figure 6.3 as a function of the *SED*. With regards to ethyl acetate, whose biodegradation in BTFs is more problematic, an energy density of 2520 J L^{-1} is required for the complete removal in the more concentrated mixture (Mixture 1.1). In Mixture 1.2, the complete removal of ethyl acetate is obtained at 1410 J L^{-1}. In Mixture 1.3, which contains low VOC concentrations, the complete removal is achieved at about 900 J L^{-1}. The *SED* needed to obtain a specific *RE* is thus strongly influenced by the initial concentration of pollutants and less concentrated streams require less energy in order to completely remove the VOCs.

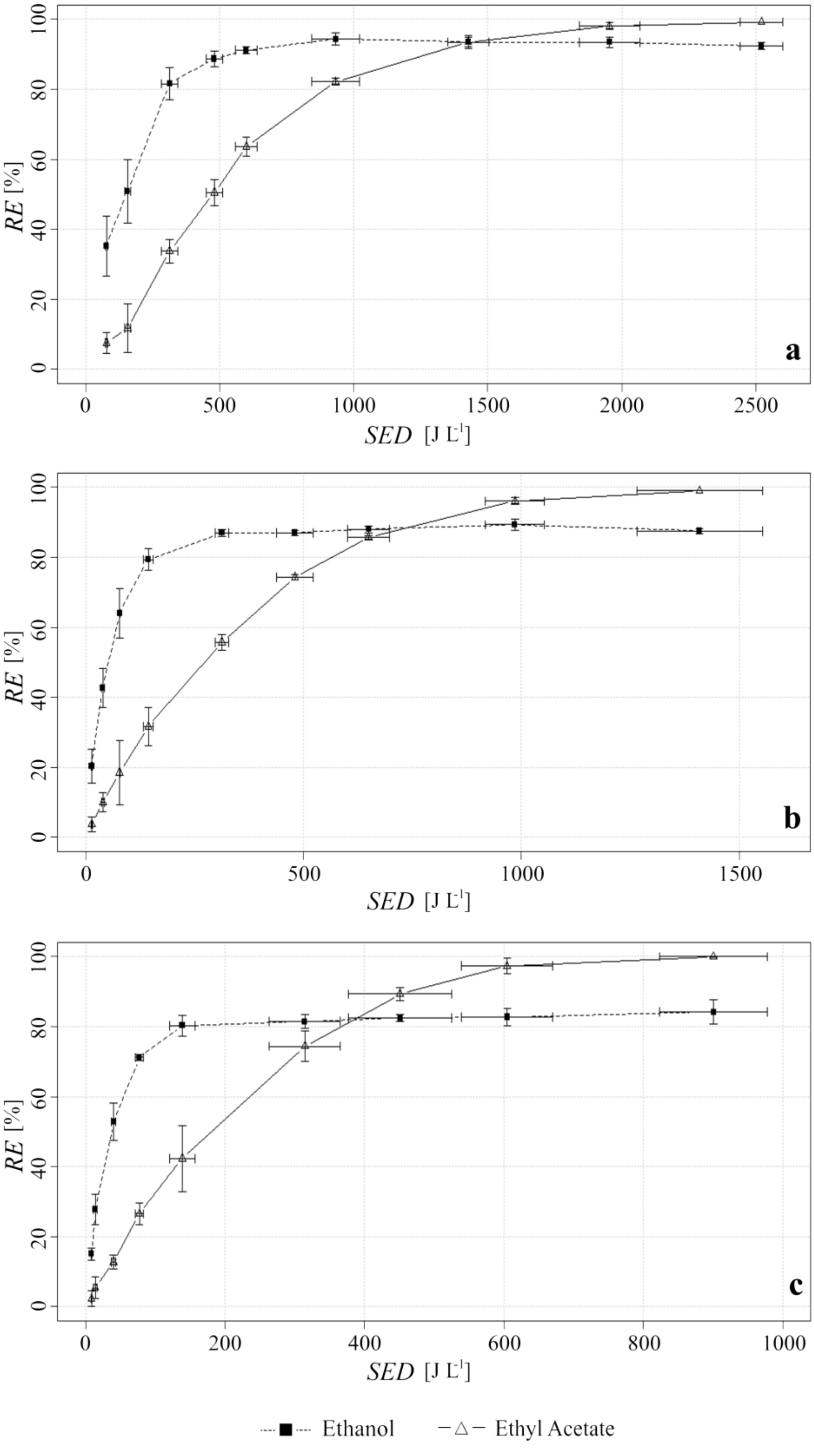

Figure 6.3: *RE*s of ethanol and ethyl acetate, as a function of the *SED*, for *a)* Mixture 1.1, *b)* Mixture 1.2 and *c)* Mixture 1.3.

Although ethanol is of secondary importance in this study, it is worth mentioning that its *RE* never exceeded 95%, within the range of energy provided during the tests. This is because ethanol might be reformed by the destruction of ethyl acetate, since the latter is an ester of acetic acid and ethanol. However, ethanol requires less energy for its conversion with respect to ethyl acetate: a 50% *RE* of ethanol was obtained with about 150 J L^{-1} (Mixture 1.1), 60 J L^{-1} (Mixture 1.2) and 40 J L^{-1} (Mixture 1.3), while the same *RE* of ethyl acetate was achieved with about 480 J L^{-1} (Mixture 1.1), 300 J L^{-1} (Mixture 1.2) and 180 J L^{-1} (Mixture 1.3). The highest *RE* of ethanol (94.3%) was achieved at 930 J L^{-1} (Mixture 1.1); at the same *SED*, the *RE* of ethyl acetate was 82.2%.

The *RE*s of benzene, toluene and octane are presented in Figure 6.4 as a function of the *SED*. The removal process is generally faster for octane and toluene than for benzene. In the case of high VOC concentrations (Mixture 2.1), the complete removal of benzene, toluene and octane requires about 2520 J L^{-1}, 1500 J L^{-1} and 1000 J L^{-1}, respectively. The *SED*s necessary for the almost-complete removal of the VOCs in the remaining mixtures are 1840 J L^{-1}, 1350 J L^{-1} and 600 J L^{-1} in Mixture 2.2, 1340 J L^{-1}, 600 J L^{-1} and 650 J L^{-1} in Mixture 2.3, 1040 J L^{-1}, 550 J L^{-1} and 580 J L^{-1} in Mixture 2.4, for benzene, toluene and octane, respectively. Within the range of energy used, RE_{max} of benzene in Mixtures 2.3 and 2.4 is 95.5% and 97.4%, respectively, while RE_{max} of octane in Mixtures 2.3 and 2.4 is 97.6% and 97.4%, respectively. The range of *SED*s investigated ensured a 100% removal of toluene in every mixture.

The results in terms of *EC* are reported in Table 6.3. As expected, EC_{max} values were higher when treating high-concentration mixtures. The highest EC_{max} values of ethanol and ethyl acetate are 4251 and 10364 g m^{-3} h^{-1}, respectively, and were achieved during the treatment of Mixture 1.1, at an *SED* of 900 and 2520 J L^{-1}, respectively. With regard to Mixture 2, the highest EC_{max} values of benzene, toluene and octane were achieved in the most concentrated mixture (Mixture 2.1) and are 837, 4790 and 6053 g m^{-3} h^{-1}, respectively. The corresponding *SED*s are comprised between 2520 J L^{-1} (with respect to benzene) and 1800 J L^{-1} (with respect to toluene and octane).

6.2.3.2 Byproducts formed during the NTP treatment

In addition to CO_2 and CO, acetic acid and acetaldehyde were formed during the NTP treatment of ethanol and ethyl acetate (Mixture 1). Acetaldehyde was generated by the oxidation of ethanol, as reported in previous studies (Wang et al., 2010; Lovascio et al., 2015). Acetic acid was formed by the destruction of ethyl acetate, the latter being the ester of ethanol and acetic acid, but its formation by a DBD treatment of the sole ethanol has also been reported (Lovascio et al., 2015). Other trace compounds were detected: methanol, formic acid, propionic acid, formamide, 2-methyl-1-propanol, 1,2-ethanediol monoformate and 1,2-ethanediol diformate. However, these compounds could not be quantified, since the chromatographic peaks could not be clearly distinguished from the background noise of the FID, due to the very low concentrations of the trace byproducts in the effluent.

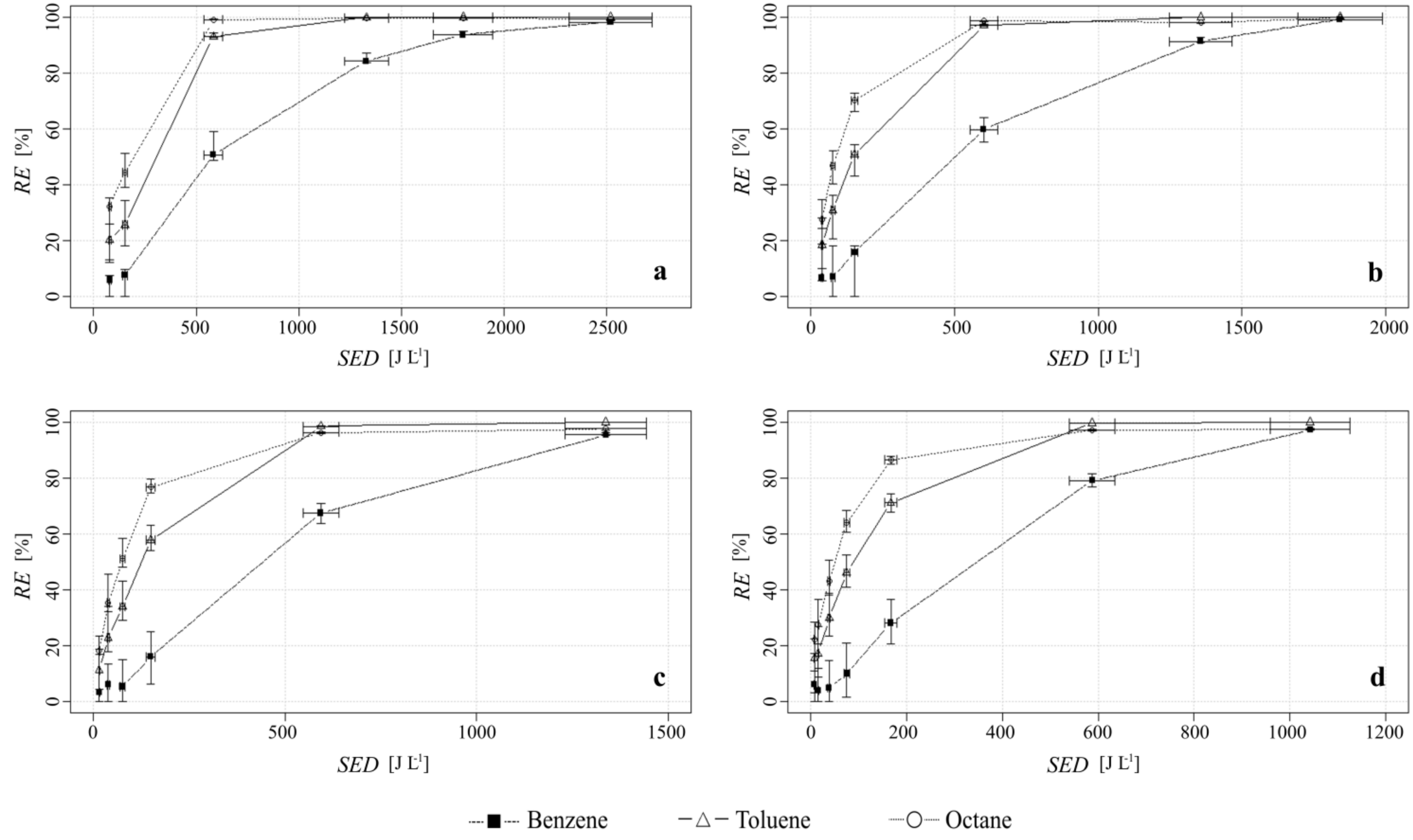

Figure 6.4: *RE*s of benzene, toluene and octane as a function of the *SED* for *a)* Mixture 2.1, *b)* Mixture 2.2, *c)* Mixture 2.3 and *d)* Mixture 2.4.

Table 6.3: EC_{max} values and corresponding REs and SEDs of each mixture of VOCs.

Mixture 1						
	Ethanol			**Ethyl Acetate**		
	Maximal EC [g m^{-3} h^{-1}]	**RE [%]**	**SED [J L^{-1}]**	**Maximal EC [g m^{-3} h^{-1}]**	**RE [%]**	**SED [J L^{-1}]**
Mixture 1.1	4251 ± 422	94.3 ± 0.6	900 ± 70	10364 ± 863	99.2 ± 0.1	2520 ± 200
Mixture 1.2	2147 ± 235	89.1 ± 1.2	990 ± 80	4724 ± 395	99.0 ± 0.1	1410 ± 110
Mixture 1.3	1369 ± 164	84.2 ± 1.7	900 ± 70	2847 ± 234	100.0 ± 0.0	900 ± 70

Mixture 2									
	Benzene			**Toluene**			**Octane**		
	Maximal EC [g m^{-3} h^{-1}]	**RE [%]**	**SED [J L^{-1}]**	**Maximal EC [g m^{-3} h^{-1}]**	**RE [%]**	**SED [J L^{-1}]**	**Maximal EC [g m^{-3} h^{-1}]**	**RE [%]**	**SED [J L^{-1}]**
Mixture 2.1	837 ± 58	98.2 ± 0.2	2520 ± 200	4790 ± 347	100.0 ± 0.0	1800 ± 145	6053 ± 433	100.0 ± 0.0	1800 ± 145
Mixture 2.2	293 ± 21	99.1 ± 0.1	1840 ± 150	2284 ± 165	100.0 ± 0.0	1360 ± 110	3157 ± 226	100.0 ± 0.0	1840 ± 150
Mixture 2.3	124 ± 10	95.5 ± 0.5	1340 ± 110	1211 ± 83	100.0 ± 0.0	1340 ± 110	1805 ± 128	97.7 ± 0.3	1340 ± 110
Mixture 2.4	69 ± 6	97.4 ± 0.3	1040 ± 80	738 ± 50	100.0 ± 0.0	1040 ± 80	1093 ± 84	97.4 ± 0.3	1040 ± 80

Acetaldehyde is the only byproduct that is included in the database of the IARC. However, acetaldehyde belongs to Group 2B, showing only limited evidence of carcinogenicity in humans (IARC, 1999). However, the maximal concentration of acetaldehyde in the effluent (151 ppm) is achieved only at a low *SED* (157 J L^{-1}) in the most concentrated mixture (Figure 6.5). Figure 6.6 presents the carbon balance at different SEDs for the three mixtures. At medium-low energies, the balance is lacking about 28% of carbon. This is probably due to the presence of lowly concentrated species or byproducts that cannot be detected or quantified by the FID. In addition, part of the missing carbon may be related to the formation of PM during the discharge, as reported in other studies (Kim, 2004; Byeon et al., 2010; Abdelaziz et al., 2013). However, no quantification of the carbon content related to aerosol formation was carried out in the studies cited; thus the possible influence of particle formation on the carbon balance cannot be estimated. At higher energies, the higher mineralization of the initial VOCs and the conversion to CO and CO_2 leads to a maximal carbon content quantifiable as 96% at the maximal *SED* applied (2520 J L^{-1}). At lower energies (0-300 J L^{-1}), the predominance of the initial VOCs and the formation of the first intermediates determine a maximal quantifiable carbon content of 100-77% (Figure 6.6).

The concentration trends of benzene, toluene and octane (Mixture 2) and of the main products of the treatment (CO and CO_2) are reported in Figure 6.7. The benzene concentration increases at low energies, since benzene is generated by the destruction of toluene (H. Huang et al., 2011). Several trace non-carcinogenic byproducts were formed when NTP was applied to Mixture 2: benzaldehyde, phenol, *o*-cresol and *p*-cresol, benzyl alcohol, isomers of octanedione and benzyloxy-benzene. In fact, benzaldehyde, benzyl alcohol and phenols have been identified in previous studies on applications of NTP to air containing benzene or toluene (Ascenzi et al., 2006; Franceschi et al., 2007; Dey et al., 2010). The trace byproducts could not be quantified, for the same reason concerning the trace compounds detected in Mixture 1.

However, by considering typical detection response factors (Scanlon and Willis, 1985), their maximal concentration in carbon can be estimated as being around 10% of the total at low *SED*s. This value decreases at medium and high *SED*s. The lack of carbon at medium-low energies was very high, due to the formation of liquid byproducts observed at the end of the treatments on the surface of the ground electrode. MS analyses indicated the presence of a high number of compounds at low concentration, thus these byproducts could not be quantified.

6.2.3.3 Selectivity to CO_2 and energy efficiency

As expected, low values of SCO_2 are achieved at low energies, due to the presence of intermediate byproducts (Subrahmanyam et al., 2010; Karuppiah et al., 2012) and to the formation of CO. The latter is generated in the presence of a low relative concentration of oxygen with respect to the initial VOC concentration (Byeon et al., 2010). Table 6.4 reports the results concerning the maximal selectivity to CO_2 for both the VOC mixtures. The highest SCO_2 related to the treatment of Mixture 1 is 70% and was achieved after treating the least concentrated mixture (Mixture 1.3) with the *SED* necessary for the complete conversion of ethyl acetate (900 J L^{-1}). SCO_2 decreases with increasing the initial VOC concentrations, since the availability of active and oxidizing species becomes limited with respect to the species to be oxidized (Byeon et al., 2010).

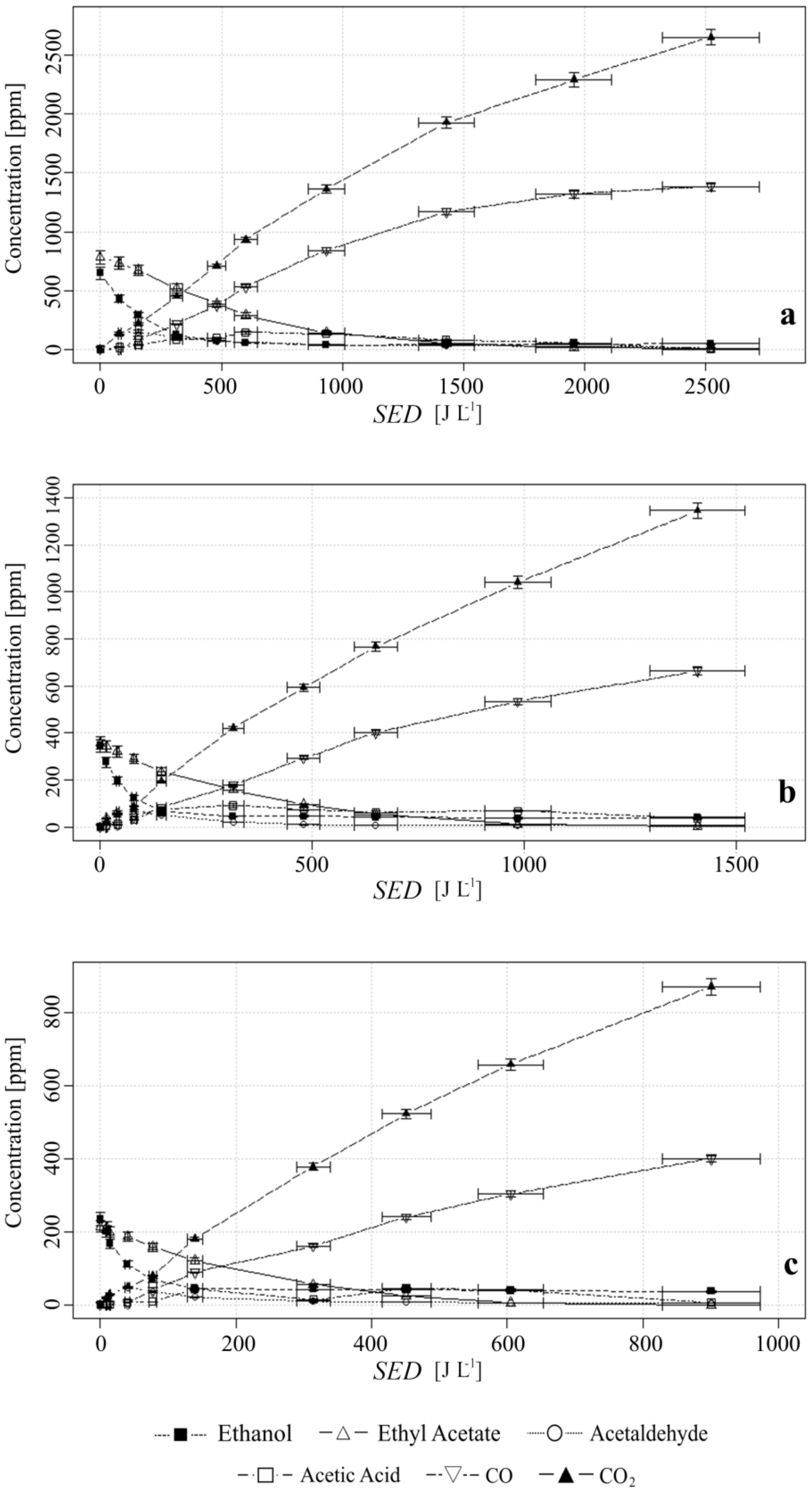

Figure 6.5: Trend of concentration of the initial compounds and byproducts in *a)* Mixture 1.1, *b)* Mixture 1.2 and *c)* Mixture 1.3, as a function of the *SED*.

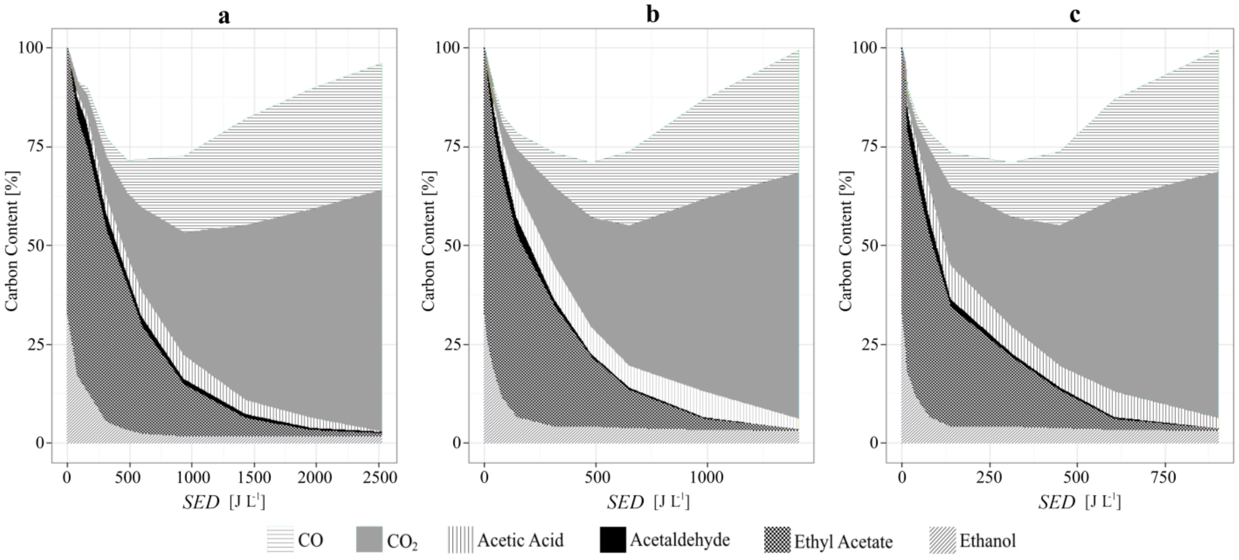

Figure 6.6: Carbon balance as a function of the SED for *a)* Mixture 1.1, *b)* Mixture 1.2 and *c)* Mixture 1.3.

The lowest SCO_2, when completely removing ethyl acetate, is 62% and was obtained when treating the most concentrated mixture (Mixture 1.1). Similar remarks can be made for Mixture 2: the lowest value of SCO_2 for total oxidation of benzene was 52%, obtained at a *SED* of 2520 J L^{-1} in the most concentrated mixture (Mixture 2.1); the highest SCO_2 was 93% and was achieved at a *SED* of 1040 J L^{-1} in the least concentrated mixture (Mixture 2.4).

The energy efficiency is strongly influenced by the initial VOC concentration. Table 6.5 reports the maximal values of *Ey* (Ey_{max}) for ethyl acetate (in Mixture 1) and benzene (in Mixture 2) for each set of initial concentrations. In spite of the lower removal efficiencies achieved when treating more concentrated mixtures, Ey_{max} increased with the initial concentration of the compounds. Thus, from the point of view of the energy efficiency, high initial VOC concentrations are preferable, as confirmed in the literature (Vandenbroucke et al., 2011). Ey_{max} obtained by treating the mixtures containing benzene (0.72 g kW^{-1} h^{-1}) was lower than other literature results on the application of a DBD, ranging from 1.5 g kW^{-1} h^{-1} (Lee et al., 2004) to 6.3 g kW^{-1} h^{-1} (Ye et al., 2008). However, these studies focused on mixtures of dry air with only benzene as a contaminant, which was present at higher initial concentrations with respect to the present study. In addition, such tests were carried out by using catalysts.

6.2.4 Conclusions

The results of the DBD treatment on the two different mixtures highlight the potential benefits of applying NTPs to different sources of VOCs. The NTP treatment with the DBD almost completely removed the VOCs chosen in this study.

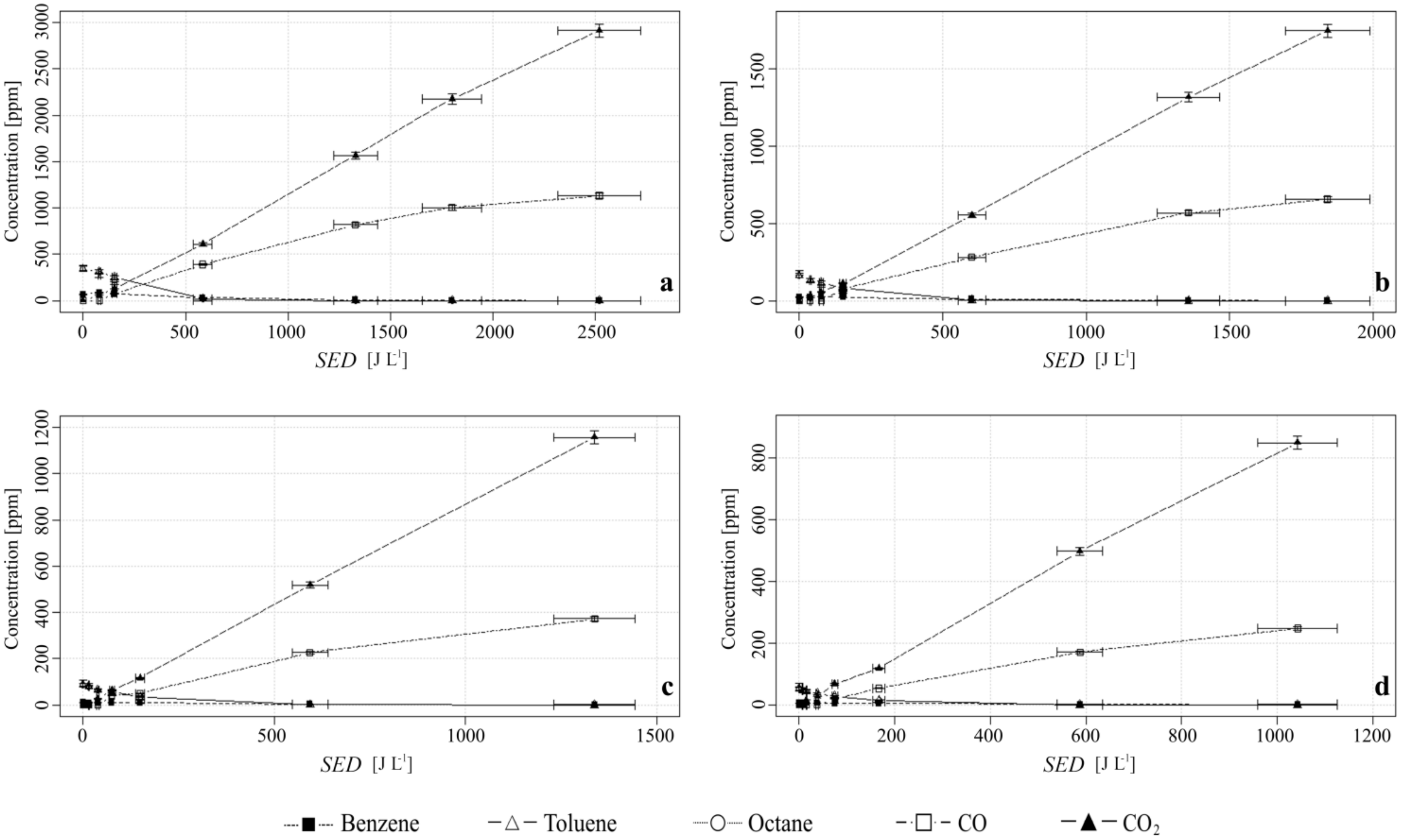

Figure 6.7: Trend of concentration of the initial compounds and byproducts in *a)* Mixture 2.1, *b)* Mixture 2.2, *c)* Mixture 2.3 and *d)* Mixture 2.4, as a function of the *SED*.

Table 6.4: CO_2 selectivity achieved at the *SED* required for complete oxidation of ethyl acetate (in Mixture 1) and benzene (in Mixture 2).

	Mixture number	SCO_2 **[%]**	***SED*** **[J L^{-1}]**
Mixture 1	Mixture 1.1	62 ± 2	2520 ± 200
	Mixture 1.2	66 ± 2	1410 ± 110
	Mixture 1.3	70 ± 2	900 ± 70
Mixture 2	Mixture 2.1	52 ± 1	2520 ± 200
	Mixture 2.2	63 ± 1	1840 ± 150
	Mixture 2.3	79 ± 2	1340 ± 110
	Mixture 2.4	93 ± 2	1040 ± 80

Table 6.5: Ey_{max} achieved during the treatment of ethyl acetate (in Mixture 1) and benzene (in Mixture 2) with different initial concentrations.

Reference VOC	**Mixture number**	Ey_{max} **[g kW^{-1} h^{-1}]**
Ethyl Acetate	Mixture 1.1	11 ± 6
	Mixture 1.2	6.0 ± 1.5
	Mixture 1.3	10.8 ± 1.6
Benzene	Mixture 2.1	0.72 ± 0.11
	Mixture 2.2	0.51 ± 0.20
	Mixture 2.3	0.27 ± 0.15
	Mixture 2.4	0.17 ± 0.10

The selected VOCs were chosen to represent typical effluents from the industrial and waste management sectors: specifically, all the selected VOCs are typical constituents of the effluents from MBTs of solid waste, while the single mixtures contain typical components of the effluents from the printing and the petrochemical industries.

The *SED*s required to obtain an *RE* higher than 95% with respect to ethyl acetate and benzene in the most concentrated mixtures (Mixture 1.1 and Mixture 2.1) were about 1500 and 2000 J L^{-1}, corresponding to a power consumption of 7.5 and 10 W, respectively. The removal process leads to the formation of oxidized species, whose degree of oxidation depends on the energy transferred to the system. For instance, at increasing energy density, ethanol is initially converted to acetaldehyde, then to acetic acid and, finally, to CO and CO_2. The formation of byproducts affects the selectivity to CO_2, which decreases when decreasing the *SED* and when increasing the initial VOC concentration.

In view of possible combinations with biofiltration technologies, one of the most encouraging results concerns the degree of polarity of the byproducts formed: the species generated are more polar than the initial compounds, thus their solubility in water is higher.

No carcinogenic compounds were found at the outlet, with the only exceptions of a possible carcinogen like acetaldehyde (in Mixture 1) and of residual benzene (in Mixture 2), both detected at medium-low *SED*s. However, providing higher *SED*s ensures a significant reduction of the carcinogenic toxicity of the outgoing mixture. In spite of these positive preliminary results, more in-depth analyses are planned for future activities to characterize the potential generation of unwanted byproducts.

The results obtained in this research activity indicate that placing an NTP treatment upstream of a biological treatment can considerably improve the removal performed by the microorganisms. NTPs are an interesting option for pre-treating VOCs in MBT plants where biological treatments are used, as well as for managing critical unsteady situations. To make the system scalable, information on *RE*s, SCO_2 and energy efficiency must be combined in order to be able to choose the most appropriate settings and configurations.

6.3 Study on the combination of NTPs with the biofiltration of VOCs

Based on: Schiavon, M., Schiorlin, M., Brandenburg, R., Torretta, V., Ragazzi, M., submitted. Non-thermal plasma assisting the biofiltration of volatile organic compounds. *Environmental Science & Technology*.

6.3.1 Introduction

VOCs are primary air pollutants that originates both from natural sources (*e.g.*, forest fires, deciduous trees) and from several types of anthropogenic activities, such as transportation, usage and production of solvents, oil refineries, chemical industry, agriculture, gas leakage from waste landfills and waste treatments (Derwent, 1995). At a European level, a 56% decrease in VOC emissions have been observed between 1990 and 2010 (European Environment Agency, 2012). The emissions from other sectors remained substantially stable during this period. The joint contributions of VOCs from industrial processes and the waste sector accounted for 8% of the total VOC emissions in 2010 (European Environment Agency, 2012). Industrial sites are generally equipped with WWTPs to recycle process water or wastewater and/or purify it before discharge into the environment (Deshmukh et al., 2015). Oil-refinery WWTPs are known sources of fugitive emissions of VOCs, especially aromatics and, more specifically, BTEX (Wei et al., 2014). Due to their volatilization, VOCs are released from wastewater and are dispersed within the atmosphere (Fatone et al., 2011). Here VOCs produce adverse effects to the environment, since they are promoters of tropospheric O_3 and contribute to the formation of radicals and aerosol (Schiavon et al., 2015b); at a local scale, VOCs can directly have adverse effects on humans by inhalation, both in terms of nuisance (due to their odour impact) and, especially, in terms of risks for health (Civan et al., 2015; Ni et al., 2015). Indeed, some VOCs are carcinogens for humans. Thus, long-term exposure to VOCs in ambient air may induce the risk of cancer both in workers and in the populations settled in the vicinity of VOC emission sources.

To reduce VOC releases from industrial WWTPs, the air of the different compartments is aspirated and treated before being released to the atmosphere. The traditional technologies for the removal of VOCs from air streams are based on physical-chemical methods, such as activated carbon adsorption, thermal or catalytic incineration and chemical scrubbing. However, such methods revealed to be unsuitable for the treatment of large air flows at relatively low concentration of contaminants (< 100 ppm), due to their impacts in terms of material and chemicals required, energy consumption, generation of waste products and related costs

(Fridman, 2008; Estrada et al., 2011). The current solution to this issue is represented by biological technologies for air pollution control. During the last decades, VOC removal and odour control at the outlet of mechanical-biological treatments of waste or wastewater treatments have been successfully achieved through biofiltration (Cabrera et al., 2011). Biofilters still represent the most convenient method to treat the stripped air from WWTPs (Dorado et al., 2015). However, as anticipated at Section 6.1, biological technologies are susceptible to unsteady conditions of flow rate and pollutant concentration, negatively influencing the adaptation time of microorganisms (Elías et al., 2010). Peaks of concentrations may also cause shock to the microorganisms responsible of biodegradation and this can affect the proper operation of a biofilter afterwards. In addition, the biodegradation of hydrophobic compounds is problematic, because of the limited diffusion of pollutants from the gaseous phase to the biofilm (Arriaga et al., 2006).

A possible solution to these typical drawbacks of biological technologies for air pollution control consists in pre-treating the gaseous effluent with a dual purpose: removing part of the inlet mass load (in the case of incoming peaks of concentrations and/or air flow rate) and increasing the solubility of the mixture of incoming pollutants. A technology based on the generation of NTP may help to achieve both these targets, in the light of the results of the laboratory experience presented in Section 6.2 (Schiavon et al., 2015d).

NTP for air pollution control and, especially, VOC removal has been the object of important laboratory-scale studies in the last years, investigating the performance of corona discharges (Schiorlin et al., 2009; Feng et al., 2015) and DBDs (Aerts et al., 2013). DBDs have also gained consideration for applications to industrial-scale air flows (Yao et al., 2004). Several studies were carried out on the application of DBDs to remove VOCs from air. Only recently, fewer studies have investigated the combination of NTPs with biological technologies for air pollution control: Wei et al. (2013) applied a BTF to remove the residual dimethyl sulphide and the byproducts formed after treating a mixture of dimethyl sulphide and compressed air with a DBD; Hołub et al. (2014) applied a DBD to ambient air, in order to generate O_3, which was used to pre-treat an effluent coming from a former biofilter.

Thus, an investigation of the effects of an NTP pre-treatment on the biodegradation of VOCs is still lacking in the literature. With the aim of filling this gap, this section focuses on a laboratory-scale activity studying the synergistic effect of NTP and biofiltration in removing a mixture of VOCs from air. A mixture of five VOCs was chosen to represent the stripping air of an industrial WWTP. After completion of the start-up phase of a laboratory-scale biofilter, a DBD was applied as a pre-treatment to take charge of an increase in the initial VOC concentrations, induced on purpose to evaluate how NTP is able to manage peaks of the inlet *ML*s of pollutants, which often occur in real cases.

6.3.2 Material and Methods

6.3.2.1 Selection of the VOC mixture

A total of five VOCs were chosen with the intention to represent a typical effluent stripped from the wastewater of a petrochemical industry. Toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene were the most abundant VOCs measured in the emissions from an existing industrial WWTP located in Sicily (Italy).

In addition to the previously mentioned impacts of VOCs released into the atmosphere, benzene and ethylbenzene are particularly important also from a toxicological point of view, since they are carcinogenic compounds: specifically, the IARC classifies benzene as a demonstrated carcinogen for humans (Group 1) and ethylbenzene as a possible carcinogen to humans (Group 2B) (IARC, 2015a). Thus, assuring a proper operation of a biofilter subject to unsteady flow conditions reveals essential to limit human exposure by inhalation and the consequent cancer risk in the population settled in the vicinity of an industrial WWTP.

All the substances were purchased from Sigma Aldrich (USA). Toluene and benzene had a purity ≥ 99.9%, while the purity of the other three compounds was ≥ 99.0%. Unavoidable fluctuations in the concentrations depended on the outdoor temperature, influencing the temperature of the compressed air used to feed the biofilter.

6.3.2.2 Experimental setup

A scheme of the experimental setup built to carry out this activity is presented in Figure 6.8 and details of the setup are reported in Figure 6.9. The experimental setup consists in four main parts:

- five bubblers for the generation of vapor-phase VOCs and one bubbler containing demineralized water for humidification of the air flow;
- the NTP unit, energized with a programmable high-voltage power source (61604, Chroma, USA) and a high-voltage transformer monitored by an oscilloscope (DPO4104, Tektronix, USA) connected to a high-voltage probe (P6015A, Tektronix, USA);
- the laboratory-scale biofilter (Air Clean Srl, Italy);
- the analytical setup, composed of a Fourier-Transform-Infrared (FTIR) spectrometer (Antaris IGS Analyzer, Thermo Scientific, USA), a GC (7890B, Agilent Technologies, USA) coupled with a single quadrupole MS detector (5977A MSD, Agilent Technologies, USA) and a Micro GC (3000 Micro GC, Inficon, Germany).

The five bubblers containing the five VOCs were fed with N_2 and each flow rate was adjusted till obtaining the desired inlet concentrations of VOCs. Two flows of compressed air were used to generate the main air flow: the first one was mixed with the five N_2 flows containing VOCs and its air flow rate was kept at 62-71 L h^{-1}; the second flow was made passing through the bubbler containing demineralized water and its flow rate was kept at 79-88 L h^{-1}; the two flows were adjusted in order to generate a total air flow rate of 150 L h^{-1} with a RH of about 50%. Each single air flow was adjusted day by day, due to the outdoor temperature variation, slightly influencing the temperature of the incoming compressed air.

The choice of working with a humid flow rate is motivated by the will to keep the experimental conditions as close as possible to real conditions: indeed, dry flow conditions are unlikely to occur when stripping air from wastewater. On the other hand, working with $RH > 50\%$ would not allow correctly quantifying the discharge power of the NTP unit. RH and the temperature of the inlet air flow were measured by means of a portable thermo-hygrometer (HP-22A, Rotronic, Switzerland). The pressure drop (ΔP) between the inlet and

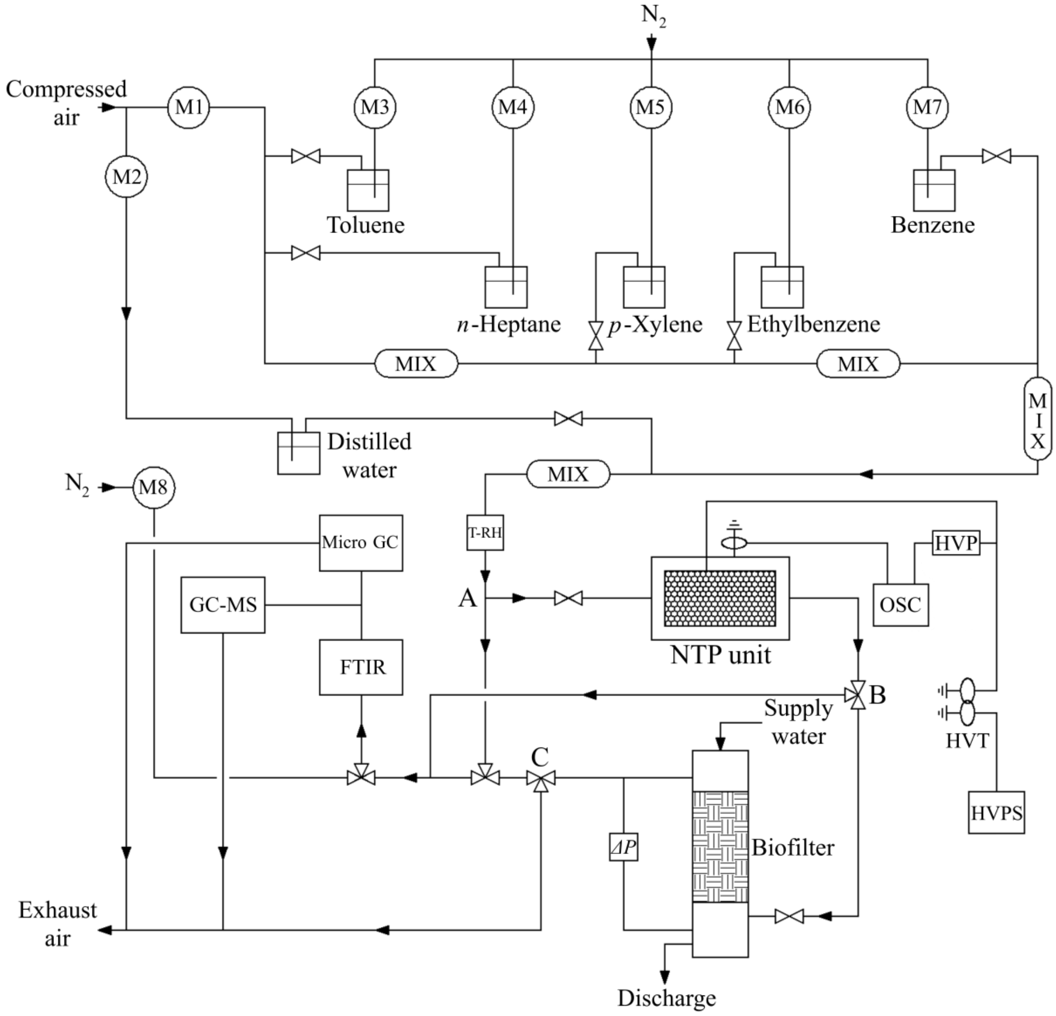

Figure 6.8: Configuration of the experimental setup (MFC: mass flow controller; MIX: mixing chamber; OSC: oscilloscope; HVP: high-voltage probe; HVT: high-voltage transformer; HVPS: high-voltage power source).

the outlet of the biofilter was kept under observation by two digital manometers (454 Data logger, Testo, Germany).

6.3.2.3 The biofilter

The laboratory-scale biofilter consists in a cylinder made of transparent PVC, with internal diameter of 0.08 m and height of 0.80 m. After being placed in the laboratory, the biofilter was filled with a specialized patented peat (Mónafil®, Bord Na Móna PLC, Ireland), till reaching a total filling height of 0.50 m. The incoming air flow enters the biofilter from the bottom, passes through the filling material and leaves the biofilter from the top. The filling material is supported by a grid, placed at 0.10 m from the bottom of the biofilter, favouring the contact between air and peat. At the flow rate investigated in this study (150 L h^{-1}), *EBRT* and *SL* are 60 s and 29.8 m^3 m^{-2} h^{-1}, respectively. Before inserting the filling material into the biofilter, the peat was mixed with a small amount of lyophilized microbial inoculum (Air Clean Srl, Italy). The inoculum con-

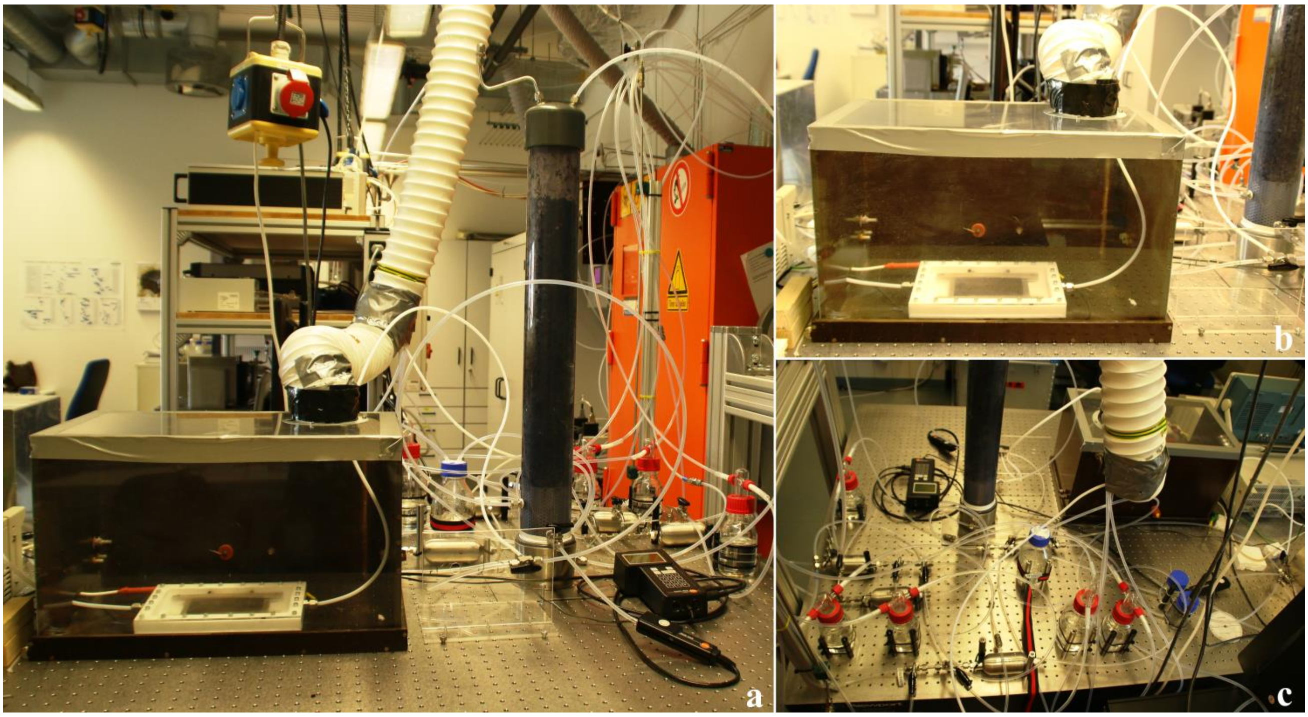

Figure 6.9: Presentation of the experimental setup with *a)* the NTP-biofilter combined system, *b)* a detail of the NTP unit and *c)* a detail of the gas lines and the bubblers.

sists in a mixture of aerobic bacteria, cultivated after extraction from the filling material of a former biofilter degrading VOCs and odorants.

6.3.2.4 The DBD

The NTP unit is composed of a single-stack DBD reactor: the high-voltage and the ground electrodes are both made of a stainless-steel mesh, while the dielectric consists in a layer of phlogopite with a thickness of 0.5 mm. The reactor is enclosed in a volume of 250 mL, providing a residence time of 6 s at the flow rate investigated in this study. To obtain indications on the energy consumption, *P* was calculated through integration of the Lissajous figure computed by the oscilloscope.

6.3.2.5 Analytical setup

The experimental setup was built in order to allow for a complete characterization of the VOC/air mixture prior to the NTP unit (sampling point A), between the NTP unit and the biofilter (sampling point B) and downstream of the biofilter (sampling point C) (Figure 6.8). Through proper regulation of the valves composing the system, the flow of interest is firstly made pass through the FTIR, is subsequently sent to the GC-MS and the Micro GC, and is finally sent to an exhaust aspiration system. The FTIR was used to quantify CO, CO_2 and the O_3 generated by the DBD; the Micro GC was used to quantify each of the 5 VOCs; the by-products of the DBD treatment were identified with the GC-MS. The Micro GC was calibrated with a gas cylinder containing dry synthetic air (20% O_2 and 80% N_2) and the five components of the VOC mixture under investigation, at reference concentrations (toluene: 100 ppm; *n*-heptane: 60 ppm; *p*-xylene: 50 ppm;

ethylbenzene: 40 ppm; benzene: 30 ppm). The mixture was purchased from Air Liquide (France). The FTIR, previously calibrated for CO and CO_2, was also calibrated for O_3, through an ozoniser (Ozomat MP, Anseros, Germany) and subsequent comparison between the areas of the O_3 peaks measured on the FTIR and the O_3 concentrations measured by an O_3 monitor. The pH of the filling material and of the water collected at the bottom of the biofilter was measured by means of the Litmus test. Microbiological analyses were also carried out on samples of filling material, in order to assess the vitality and the type of the microorganisms involved in the VOC biodegradation.

6.3.2.6 Biofilter start-up

To allow for a proper growth of the bacteria initially present in the inoculum, biofilters require a startup phase of several weeks. During this phase, the *ML* is gradually increased till reaching stable removal performance. In this study, the initial VOC concentrations were increased at the design air flow rate (150 L h^{-1}). The biofilter was initially fed with only toluene, starting from a concentration of about 30 ppm. The biofilter was daily monitored and, every time the biofilter reached a *RE* > 90%, the initial concentration was subsequently increased till reaching a target concentration. Afterwards, a new compound was added to the mixture and the same procedure was followed with the remaining VOCs. During the start-up phase, the air temperature remained comprised between 24.0 and 25.6 °C.

A proper humidification of the filtering medium was assured by the partially humidified air flow and by regular addition of 100 mL of water every 72 h. After completion of the start-up phase, this interval was increased to 96 h. Except from water, no nutrient solution was added to the biofilter during the whole period.

6.3.2.7 Test procedure

After the completion of the start-up phase, the air flow rate was kept constant at 150 L h^{-1} and the inlet VOC concentrations were kept as close as possible to the average concentrations reached at the end of the start-up phase.

To test the application of NTP in pre-treating increases in the VOC concentrations and, meanwhile, not to stress the microorganisms in the biofilter, the following test procedure was implemented: the rates of the N_2 flows feeding the bubblers containing the five VOCs were increased by 25%; the VOC concentrations in the air flow consequently increased; the NTP was activated and the energy provided to the discharge was gradually increased to the energy necessary to obtain again the initial total concentration of the five starting VOCs (about 290 ppm) at the inlet of the biofilter. This way, the DBD can be studied as a pre-treatment option to reduce peaks of concentrations and to level the concentrations in the flow exiting the DBD to the values the biofilter was acclimated at. Keeping the concentrations constant at the inlet of the biofilter would preserve microorganisms from shock, would allow for a proper operation of the biofilter and would not negatively affect its *RE*. Meanwhile, the efficiency and the energy consumption of the DBD can be tested.

After carrying out these tests, the same procedure was repeated with increasing the rates of the N_2 flows feeding the bubblers containing VOCs by 50% and 100%. All the errors were determined by the error propagation formula, considering the instrumental and calibration errors.

6.3.3 Results and discussion

6.3.3.1 Biofilter start-up

Four days after the start-up of the biofilter, the *RE* of toluene became close to 90%, so that the initial concentration was increased to about 70 ppm. After 9 d of operation, the biofilter was capable to degrade toluene at the final concentration of 95.6 ppm with a 99% *RE*. Afterwards, *n*-heptane was inserted into the mixture at an initial concentration of 25 ppm. 25 d later, a 99% *RE* was obtained and, then, its inlet concentration was increased to 49.4 ppm. *p*-Xylene, ethylbenzene and benzene were added to the system one by one, after that *RE*s > 99% had been reached with regards to every new VOC introduced. At the end of the start-up phase, the average concentrations of the single VOCs at the inlet of the biofilter resulted as 95.6 ppm of toluene, 49.4 ppm of *n*-heptane, 60.8 of *p*-xylene, 47.3 ppm of ethylbenzene and 36.6 ppm of benzene.

The acclimation period of the microorganisms present in the biofilter to these three VOCs was particularly short: indeed, after a total time of 30 d of operation, the biofilter became fully operative and the *RE* was > 99% for all the VOCs in the mixture, with the only exception of *n*-heptane. The inlet VOC concentrations and their *RE*s during the start-up phase of the biofilter are reported in Figure 6.10.

Microbiological analyses on samples of peat revealed that the microorganisms present in the filling material belonged to the *Pseudomonas* and *Bacillus* strains. The cell count at the end of the start-up phase resulted in $3.95 \cdot 10^5$ CFU g^{-1} of dry material. During the whole period of operation of the biofilter, the maximal ΔP between B and C resulted in 40 mmH_2O.

6.3.3.2 Application of NTP

After increasing the N_2 flow rates of every VOC line by 25%, 50% and 100%, the inlet VOC concentrations changed to the values reported in Table 6.6. The *SED* provided to the discharge was gradually increased from 46 J L^{-1} to 128 J L^{-1}, from 49 J L^{-1} to 165 J L^{-1} and from 92 J L^{-1} to 256 J L^{-1}, in the case of a 25%, 50% and 100% increase of N_2 flow rates feeding the bubblers containing the initial VOCs, respectively. At every increase in the energy provided to the DBD, the VOC concentrations were continuously monitored both at the sampling point B and at the sampling point C, in order to assess both the performance of the only NTP treatment and of the NTP-biofilter combined system. The VOC concentrations at the outlet of the NTP unit (B), at the different *SED*s investigated, are reported in Figure 6.11. Hereinafter, for an easier view of the graphs, the errors associated with *SED* (estimated as equal to 8% of the value) will be omitted.

As expected, at higher *SED* the VOC concentrations after the NTP treatment tend to decrease due to the conversion of the initial compounds operated by the DBD. However, a threshold *SED* of 70-125 J L^{-1} can be observed before the initial VOCs start to be decomposed. This can be explained by the presence of humidity in the air flow: part of the energy provided to the DBD is dissipated through excitation of the vibrational levels and polarization of water molecules.

The VOC showing smaller degradation is benzene, which seems to be even reformed at a *SED* comprised between 95 J L^{-1} (in the case of a 25% increase of the N_2 flow rates feeding the bubblers containing the initial VOCs) and 125 J L^{-1} (in the case of a 100% increase). This is consistent with the previous activity carried

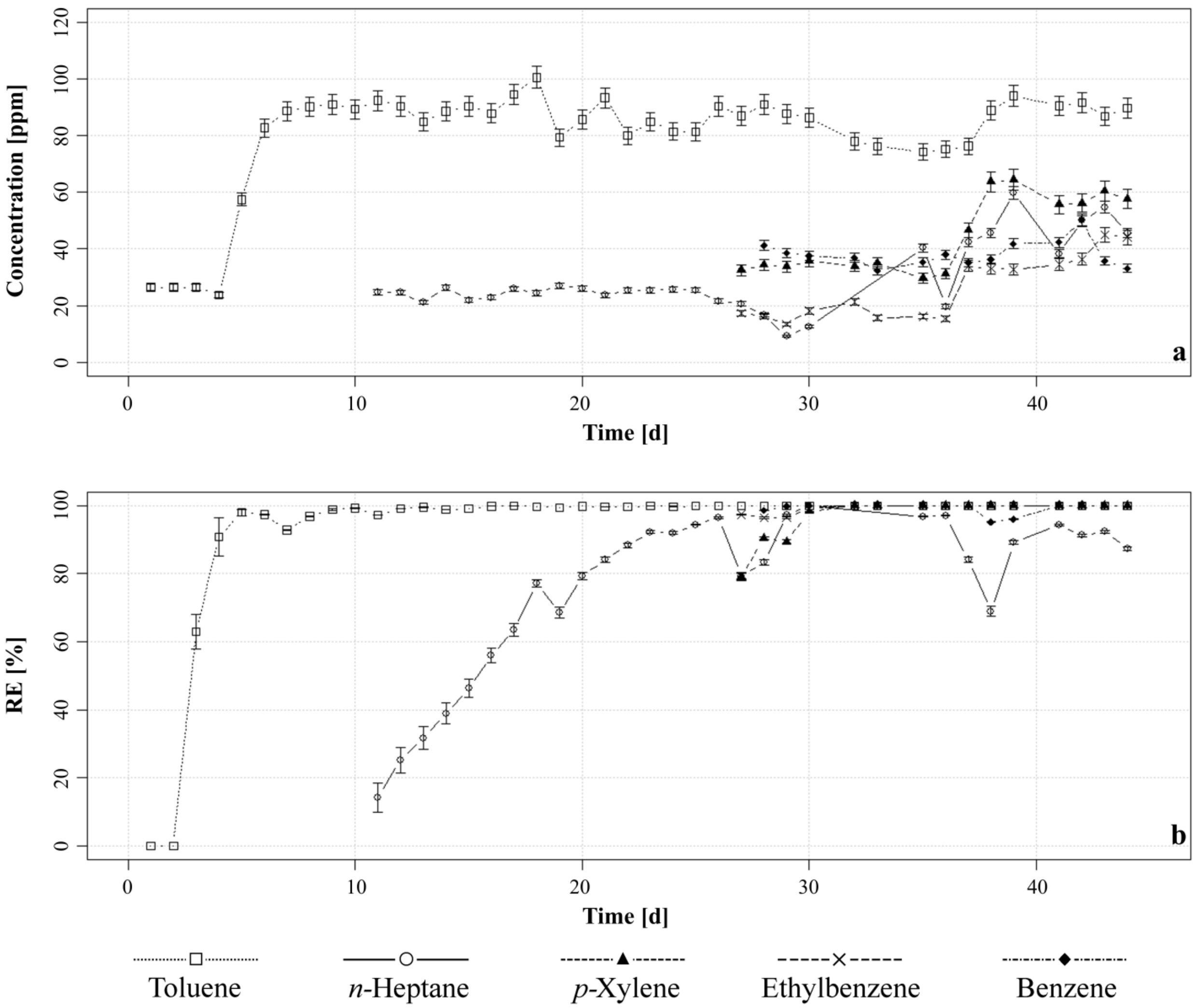

Figure 6.10: Trends *a)* of the VOC concentrations at the inlet of the biofilter and *b)* of the respective *RE*s during the start-up phase of the biofilter.

out on the mixture of toluene, benzene and *n*-octane (Schiavon et al., 2015d) presented at Section 6.2, where the reformation of benzene was ascribed to toluene degradation operated by NTP. At the maximal *SED*s investigated, the concentrations of every VOC at the inlet of the biofilter (B) were close to the inlet concentrations achieved at the end of the start-up phase, thus before any tests with plasma.

Benzaldehyde, acetophenone, styrene and formic acid were detected as the main organic byproducts of the NTP degradation of the VOCs initially present in the mixture. At increasing *SED*, the formation of such byproducts is more and more reduced. All the byproducts formed are more water-soluble than the initial VOCs. This results is in line with what found in the previous study presented at Section 6.2 (Schiavon et al., 2015d).

In addition, at the outlet of the NTP unit, the carcinogenic potential of the mixture is reduced, since it is related only to residual benzene and ethylbenzene, and to traces of styrene (generated by the application of NTP), classified in the Group 2B by the IARC (IARC - International Agency for Research on Cancer, 2015a) and not classified as a carcinogen by the US EPA (US EPA, 2015c). NTP generated a maximal O_3 concen-

Table 6.6: VOC concentrations (expressed as ppm) measured at the sampling point A, before and after each increase in the VOC flow rates.

		Toluene	***n*-Heptane**	***p*-Xylene**	**Ethylbenzene**	**Benzene**
25% increase	Before	101.0 ± 3.9	52.5 ± 1.9	68.3 ± 3.9	47.9 ± 2.7	39.4 ± 1.7
	After	125.7 ± 4.8	63.9 ± 2.3	85.1 ± 4.9	62.1 ± 3.6	47.3 ± 2.0
50% increase	Before	94.4 ± 3.6	48.3 ± 1.8	58.7 ± 3.4	46.1 ± 2.6	36.9 ± 1.6
	After	140.3 ± 5.4	71.0 ± 2.6	88.1 ± 5.0	73.4 ± 4.2	53.3 ± 2.3
100% increase	Before	91.3 ± 3.5	47.5 ± 1.7	55.4 ± 3.2	47.9 ± 2.7	33.6 ± 1.5
	After	182.3 ± 7.0	98.3 ± 3.6	126.5 ± 7.2	96.5 ± 5.5	70.3 ± 3.0

tration of 250 ppm, which is considered tolerable by microbial populations (Wang et al., 2013). The maximal CO_2 concentrations generated by NTP were achieved at the maximal *SED* applied, and varied between 333 and 840 ppm in the case of a 25% and a 100% increase in the VOC flow rates, respectively. The DBD also generated maximal CO concentrations of 227 and 504 ppm, after increasing the VOC flow rates by 25% and 100%, respectively.

The overall *RE*s of the five initial VOCs after the combined NTP-biofilter treatments at increased VOC concentrations are presented in Figure 6.12 as a function of the *SED* applied. At the maximal *SED*s used (128, 165 and 256 J L^{-1}, in the case of a 25%, 50% and 100% increase in the N_2 flow rates, respectively), the *RE*s of the initial VOCs were > 93%, with the only exception of *n*-heptane, whose maximal *RE*s varied in the range 81-91%, the lowest value being referred to the case with a 100% increase in the VOC flow rates. Such value is anyway in line with the *RE* of *n*-heptane obtained with the only biofilter before increasing the initial VOC concentrations. In confirmation of the fact that the biofilter alone was not enough to assure satisfying *RE*s after increasing the *ML*s of the five VOCs, the *RE* of the biofilter was assessed after switching off the DBD, at the end of the test with N_2 flow rates increased by 100%, before lowering the VOC concentrations to the initial values: in such conditions, the *RE*s of toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene were 60%, 23%, 87%, 76% and 28%, respectively.

The CO concentration at the outlet of the biofilter was found to be up to 10% lower than its concentration after the NTP unit. This suggests that part of CO, toxic to several bacterial strains, may have been metabolized by the microorganisms, with possible poisoning.

The cell count at the end of all the tests with NTP resulted in $2.95 \cdot 10^5$ CFU g^{-1} of dry material, *i.e.*, 25% lower than the value measured at the end of the start-up phase of the biofilter. As a solution to this possible criticality, CO could be treated in a first biofilter stage inoculated with CO-degrading populations under aerobic conditions, *e.g.*, the *Pseudomonas carboxydovorans* (Meyer and Schlegel, 1978). However, such decrease in the cell count might also be attributed to two additional causes: the temporary unavoidable stress to bacteria during the transient phase between the concentration increases and the adjustment of the NTP unit to reach optimal removal conditions; the absence of micronutrients supplied to the microorganisms. With regard to the NTP treatment alone, the SCO_2 calculated at the highest *SED* resulted in 41% (*SED* = 128 J L^{-1}), 41% (*SED* = 165 J L^{-1}) and 43% (*SED* = 256 J L^{-1}) after a 25%, 50% and 100% increase in the *ML*s, respectively.

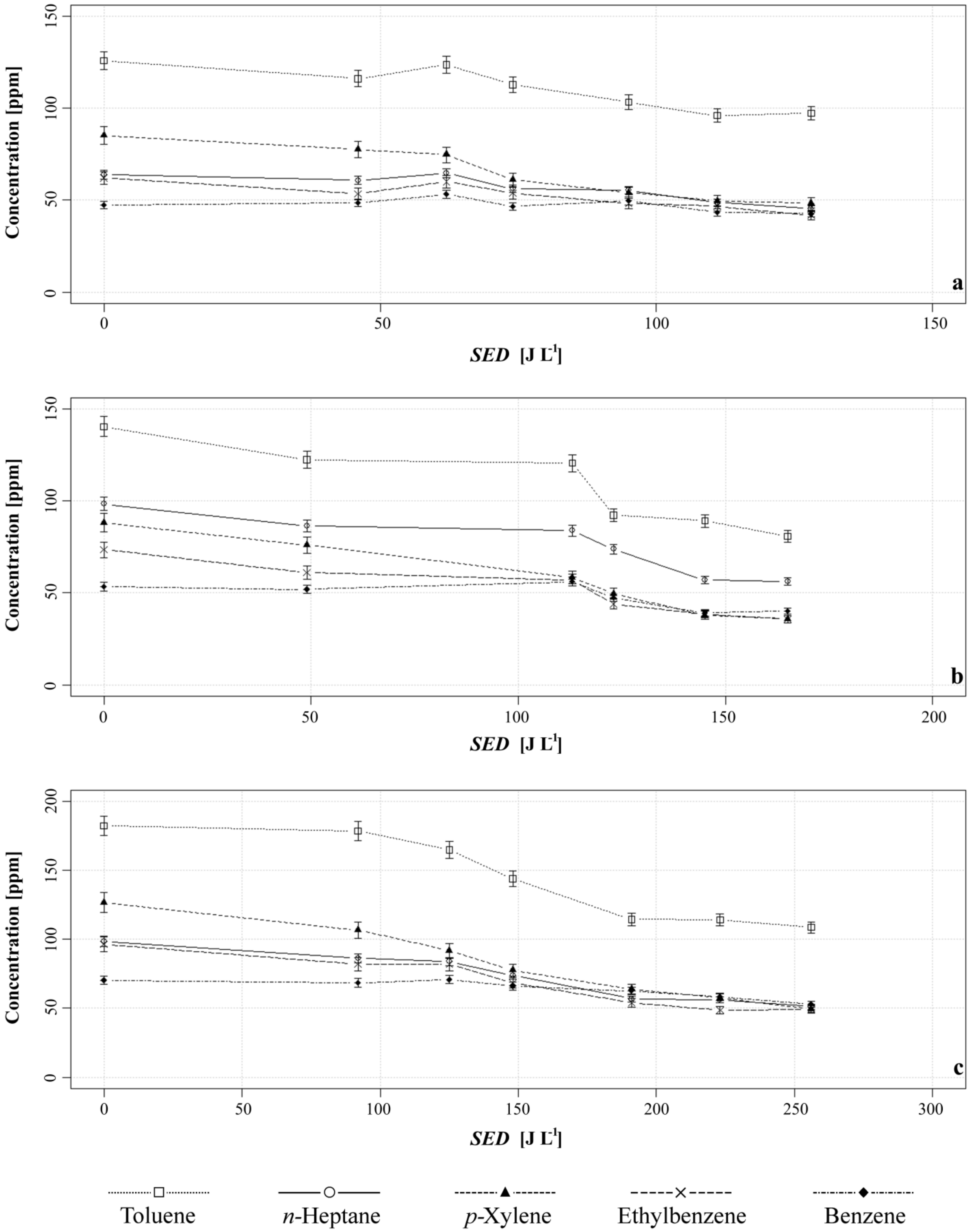

Figure 6.11: VOC concentrations measured in B as a function of the *SED* during the tests with a *a)* 25%, *b)* 50% and *c)* 100% increase in the N_2 flow rates feeding the bubblers containing VOCs.

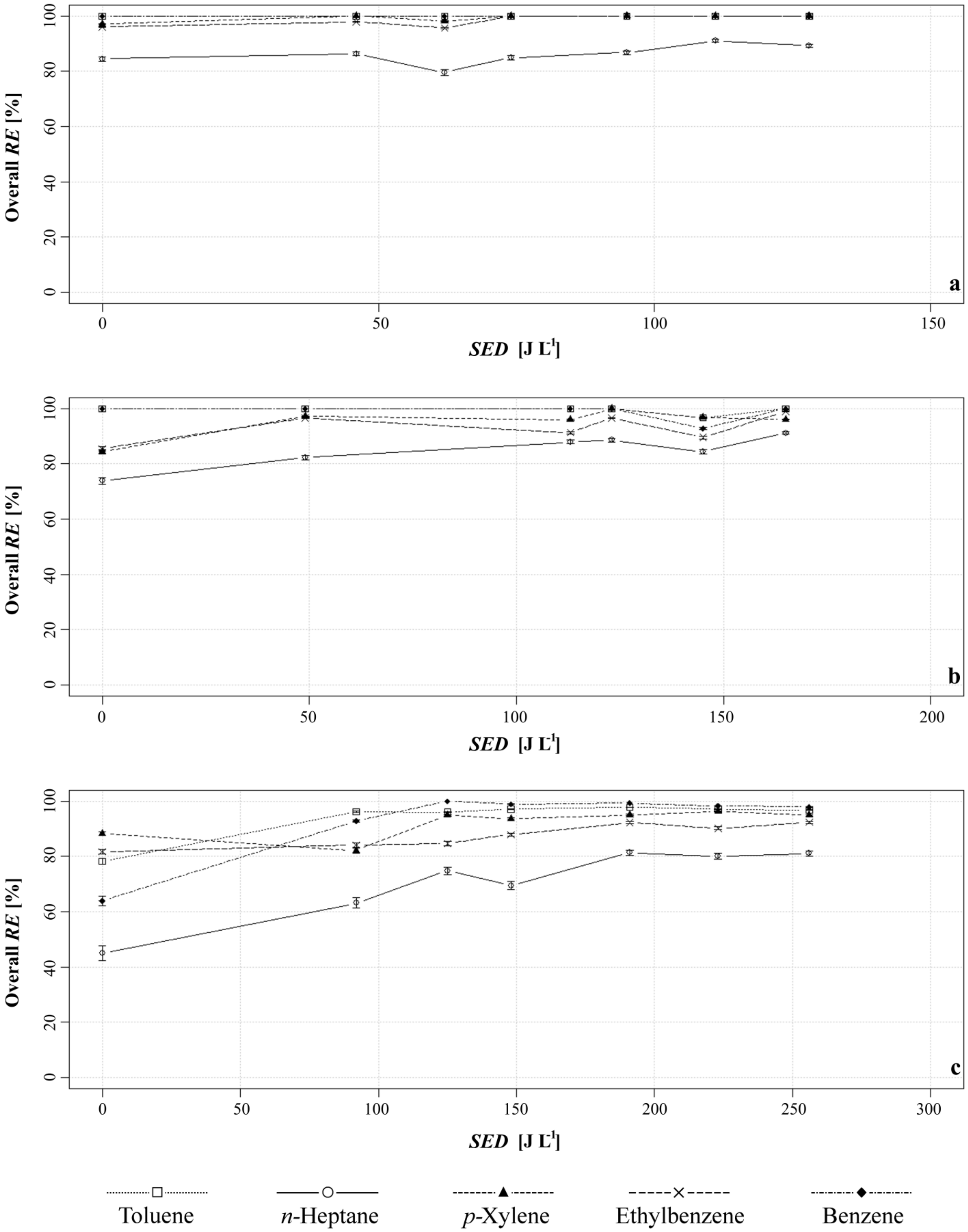

Figure 6.12: Overall *RE*s of the five reference VOCs after the combined NTP-biofilter treatment with a *a)* 25%, *b)* 50% and *c)* 100% increase in the initial VOC concentrations.

The EC_{max} of the five initial VOCs during each of the three tests are reported in Table 6.7 together with the respective *SED*s and *ML*s. Since the tests were carried out by gradually increasing the *SED* with the aim of achieving satisfying overall *RE*, EC_{max} increases with increasing the *ML*. In the case of toluene and benzene, after a 25% and 50% increase in the N_2 flow rates, EC_{max} was achieved with the biofilter alone, which assured almost complete removal of these compounds.

The highest values of EC_{max} were achieved by toluene (24.40, 37.75 and 49.02 g m^{-3} h^{-1} after increasing the N_2 flow rates by 25%, 50% and 100%, respectively), which is the most concentrated VOC in the mixture. The lowest EC_{max} values were achieved by benzene (9.05, 10.37 and 13.72 g m^{-3} h^{-1} after increasing the N_2 flow rates by 25%, 50% and 100%, respectively), which is the least concentrated VOC. Although the *ML*s of the remaining VOCs are similar, EC_{max} increases when moving from *n*-heptane to ethylbenzene and, finally, to *p*-xylene.

Table 6.8 presents the Ey_{max} obtained for each VOC after the NTP treatment, the respective *SED*, the corresponding overall *RE* of the NTP-biofilter combined treatment, the respective *RE* of the NTP treatment alone (RE_{NTP}) and the maximal *RE* of the NTP treatment alone ($RE_{NTP,max}$) achieved within the range of *SED* investigated in each test with increased initial concentrations. From the point of view of energy consumption, the most difficult compound to be degraded by NTP is benzene, whose degradation requires more energy than the other VOCs in the mixture. In analogy with EC_{max} (Table 6.7), benzene is followed by *n*-heptane, ethylbenzene, *p*-xylene and toluene, which gradually allow for higher *Ey*.

In general, the more the initial compounds are concentrated (*e.g.*, after a 100% increase in the N_2 flow rates), the higher Ey_{max} is. In fact, at higher initial concentrations, the probability of reaction between O_3 and radicals with the initial compounds increases. Two exceptions are here represented by toluene and benzene, whose Ey_{max} after a 50% increase of the N_2 flow rates is 5.29 and 1.12 g kWh^{-1}, respectively, while the re-

Table 6.7: EC_{max} of the biofilter and corresponding *ML* and *SED* of the five reference VOCs achieved during the three tests with a 25%, 50% and 100% increase in the VOC flow rates (*ML* and EC_{max} are expressed as g m^{-3} h^{-1}, *SED* is expressed as J L^{-1}).

		25% increase	50% increase	100% increase
Toluene	EC_{max}	28.40 ± 1.09	31.69 ± 1.22	40.27 ± 1.55
	ML	28.40 ± 1.09	31.69 ± 1.22	41.18 ± 1.58
	SED	0 ± 0	0 ± 0	191 ± 8
***n*-Heptane**	EC_{max}	14.30 ± 0.54	15.90 ± 0.59	16.95 ± 0.74
	ML	15.70 ± 0.58	17.43 ± 0.64	24.15 ± 0.89
	SED	111 ± 4	165 ± 7	191 ± 8
***p*-Xylene**	EC_{max}	22.16 ± 1.27	22.93 ± 1.31	31.69 ± 1.82
	ML	22.16 ± 1.27	22.93 ± 1.31	32.91 ± 1.88
	SED	46 ± 2	123 ± 5	223 ± 9
Ethylbenzene	EC_{max}	16.16 ± 0.92	18.89 ± 1.08	23.21 ± 1.34
	ML	16.16 ± 0.92	19.09 ± 1.09	25.12 ± 1.44
	SED	74 ± 3	165 ± 7	191 ± 8
Benzene	EC_{max}	9.05 ± 0.39	10.20 ± 0.44	13.46 ± 0.58
	ML	9.05 ± 0.39	10.20 ± 0.44	13.46 ± 0.58
	SED	0 ± 0	0 ± 0	125 ± 5

Table 6.8: Ey_{max} and corresponding *SED*, overall *RE*, RE_{NTP} and $RE_{NTP,max}$ of the five reference VOCs obtained during the three tests with increased initial concentrations (Ey_{max} is expressed as g kWh^{-1}, *SED* in J L^{-1} and *RE*s in percentage).

		25% increase	**50% increase**	**100% increase**
Toluene	Ey_{max}	3.63 ± 0.87	5.29 ± 0.92	4.82 ± 0.78
	SED	111 ± 4	123 ± 5	191 ± 8
	overall *RE*	100.0 ± 0.0	100.0 ± 0.0	97.8 ± 0.1
	RE_{NTP}	23.7 ± 3.8	34.3 ± 3.3	37.3 ± 3.1
	$RE_{NTP,max}$	23.7 ± 3.8	42.4 ± 2.9	40.5 ± 3.0
***n*-Heptane**	Ey_{max}	2.13 ± 0.43	3.17 ± 0.44	3.20 ± 0.47
	SED	128 ± 5	145 ± 6	191 ± 8
	overall *RE*	89.2 ± 0.5	84.4 ± 0.8	81.4 ± 0.9
	RE_{NTP}	28.9 ± 3.6	44.0 ± 2.8	42.2 ± 2.9
	$RE_{NTP,max}$	28.9 ± 3.6	45.5 ± 2.7	48.0 ± 2.6
***p*-Xylene**	Ey_{max}	5.09 ± 1.14	5.39 ± 0.73	5.15 ± 1.09
	SED	74 ± 3	145 ± 6	148 ± 6
	overall *RE*	100.0 ± 0.0	96.7 ± 0.2	93.7 ± 0.5
	RE_{NTP}	28.4 ± 3.6	57.0 ± 2.2	38.6 ± 4.4
	$RE_{NTP,max}$	43.1 ± 2.8	59.4 ± 2.0	60.7 ± 2.8
Ethylbenzene	Ey_{max}	2.95 ± 1.19	3.95 ± 1.36	3.49 ± 0.56
	SED	46 ± 2	49 ± 2	191 ± 8
	overall *RE*	97.9 ± 0.1	96.6 ± 0.2	92.3 ± 0.4
	RE_{NTP}	14.0 ± 4.3	16.9 ± 4.2	44.1 ± 2.8
	$RE_{NTP,max}$	32.9 ± 3.4	51.5 ± 2.4	49.5 ± 2.5
Benzene	Ey_{max}	0.41 ± 0.26	1.12 ± 0.25	0.78 ± 0.18
	SED	111 ± 4	145 ± 6	256 ± 10
	overall *RE*	100.0 ± 0.0	92.8 ± 0.4	97.9 ± 0.1
	RE_{NTP}	8.2 ± 4.6	26.6 ± 3.7	24.6 ± 3.8
	$RE_{NTP,max}$	9.6 ± 4.5	26.6 ± 3.7	24.6 ± 3.8

spective Ey_{max} reduces to 4.82 and 0.78 g kWh^{-1} after a 100% increases of the N_2 flow rates. The overall *RE* corresponding to Ey_{max} is always > 92%, with the exception of *n*-heptane, whose overall RE is equal to 89% 84%, and 81% when increasing the VOC flow rates by 25%, 50% and 100%, respectively.

6.3.4 Conclusions

As a result of these tests, NTP reveals as a promising technology to pre-treat a VOC-containing effluent during increases in the *ML* that may compromise the proper operation of a biofilter. Satisfying overall *RE*s were obtained with relatively low energy consumption, since the maximal *SED* used was 256 J L^{-1}.

Although performance parameters like EC_{max} and Ey_{max} are partially influenced by the initial VOC concentrations, a ranking of the VOCs most difficult to be abated by NTP and by the combined NTP-biofilter system can be anyway drawn up: benzene resulted as the more energy-demanding and, in general, less degradable VOC, followed by *n*-heptane, ethylbenzene, *p*-xylene and toluene. NTP, in addition to help keeping the concentrations constant at the inlet of the biofilter (in spite of the increases in the concentrations induced on purpose), demonstrates to be capable of generating byproducts that are more soluble than the initial VOCs and this could further help the biodegradation operated by biofiltration systems. Finally, the byproducts formed during these tests are less toxic than the initial VOCs. However, a 25% decrease in the microbial cell number was observed during the tests, probably because of poisoning effects of the CO generated by the DBD, the need for nutrients by microorganisms and the stress to the microbial populations provoked during the attempts to adjust the energy provided to the DBD till reaching satisfying *RE*s. In view of future applications, the primary removal of the CO generated by plasma, the supply of nutrients and the optimization of the adjustment of the NTP settings should be pursued. In addition, further investigation is needed to reduce the energy costs expected when scaling up an NTP unit for pilot- or industrial-scale applications. The research should focus on the optimization of the discharge, both in terms of type of discharge (corona or DBD discharges) and in terms of contact between the effluent and ionized species, radicals and electrons.

7 Conclusions and outlook

During this doctoral research, several aspects of the same problem were investigated and different methodological and technical solutions were proposed, as an answer to the need for strategies that minimize the impacts of underestimated emission sources and pathways of exposure to atmospheric pollutants.

7.1 Synthesis of the results obtained

After introducing the issues related to the effects of air pollution on human health and identifying carcinogenic organic air contaminants as the priority pollutants, Chapter 2 presented potential critical situations of exposure, especially concerning activities and pathways of exposure whose effective impacts on health are normally not adequately considered by the population and the current environmental legislation. Open issues regarding both the lack of regulations for some activities and the inadequacy of some conventional monitoring approaches were described, with specific attention to two of the most potent carcinogenic air pollutants: dioxin and benzene. Proposals for integrative monitoring techniques and novel methodologies for exposure assessment were then presented, with the purpose of offering alternative options to reduce costs without losing the capability of detecting anomalies in the exposure. In the case of dioxin, integrative methodologies to food inspections and soil concentrations are represented by passive sampling and biomonitoring techniques (based, for instance, on sewage sludge characterization, analyses on conifer needles and lichens), dispersion modelling and the coupling of atmospheric deposition monitoring with food-chain models. In the case of benzene and VOCs, the low spatial resolution of fixed air quality stations could be improved by introducing networks of wireless sensors and/or passive samplers, whose location can be chosen on the basis of simulations of dispersion in the atmosphere.

Four integrative methodologies, developed during this doctoral research, were presented in Chapter 3. The first one concerns the assessment of anomalies in the exposure to dioxin through analysis of the sewage sludge of WWTPs; this methodology recently received attention from APPA Trento. The second and third methodologies give value to two monitoring techniques (deposition and sediment samplings) whose environmental matrixes are not uniformly regulated in terms of dioxin content; atmospheric deposition of POPs on farmlands and pastures, especially, can lead to accumulation of such contaminants in the diet; its quantification becomes then important to estimate the intake of dioxin through ingestion of contaminated food or, as presented in Chapter 4, to assess the compliance with an acceptable deposition value that preserves the diet; in addition, the evaluation of the congener distribution and the calculation of diagnostic ratios revealed as suitable tools to identify the dominant sectors responsible for POP contribution in an area. The fourth methodology here presented gives value to the dispersion modelling chain, as a tool to locate critical situations of exposure where the conventional monitoring approach cannot supply information, as a tool to evaluate the sectors that most contribute to the air quality of an area and as an aid for urban/environmental planners and decision makers to locate sensitive activities (*e.g.*, schools and hospitals) and adopt mitigation strategies.

A proposal for a limit value for atmospheric deposition of PCDD/Fs to soil was presented in Chapter 4, along with the methodology developed. This methodology moves from consolidated food-chain models, originally developed to estimate the accumulation of PCDD/Fs in food, on the basis of its deposition and its concentration in soil and ambient air. The methodology here presented runs the food chain backwards, since it starts from the TDI proposed by the WHO, rearranges the food-chain models and, finally, allows estimating a tolerable deposition value to preserve the diet of a population. The application of this methodology to different populations would result in different guide values, since such methodology greatly depends on the food habits and on the average food consumption of a population. Such method represents an attempt to overcome the current absence of regulatory limit values for atmospheric deposition of PCDD/Fs to soil in several countries. This approach aims at reducing the potential exposure to dioxin by preventing excessive intake and by acting at the receptor level, *i.e.*, the human body. In summary, food coming from an area where the PCDD/F deposition is lower than the guide value would preserve the diet of the reference population from an unacceptable daily intake of PCDD/Fs.

In Chapter 5, a critical analysis was carried out on biofilters, widely used to treat air streams with low concentrations of VOCs. The introduction of quality parameters on the evaluation the PCDD/F deposition in the surroundings of a hypothetical bio-stabilization plant allowed pointing out the impacts expected in the vicinity of the plant when conventional biofilters are adopted instead of other APC solutions. Indeed, based on validated emission factors and dispersion simulations, biofilters cannot guarantee a proper dilution of the plume in the atmosphere, due to intrinsic design reasons, namely the large surface required, the consequent low velocity of the effluent released and the low release height. Similar conclusions were drawn after a second set of simulations on a model odorant (DMDS) and a model carcinogen (benzene) released by a bio-drying plant equipped with a conventional biofilter. The benefits deriving from the adoption of an APC system that allows conveying the plume and releasing the effluent at a higher point were quantified by replacing the biofilter with four equivalent BTFs assuring the same *RE*. The more compact size of BTFs allows releasing the effluent at higher velocity; in addition, a conveying system can be easily installed to increase the release height. Thus, BTFs can be a low-cost and biological alternative to conventional biofilters. Their characteristics and expected performance were presented in detail in a comprehensive review concerning laboratory-scale applications to different kinds of pollutants. The optimization of APC technologies allows reducing exposure by acting directly at the emission level rather than at the receptor level.

The same aim was pursued in Chapter 6, in which an innovative VOC removal technology, based on NTP, was proposed. Two laboratory activities were presented: initially, NTP was applied to treat two mixtures of air and VOCs, chosen to represent typical emissions from real industrial activities: a printing house and the wastewater treatment of a petrochemical plant; the positive results in terms of VOC removal, especially of benzene (carcinogenic compound) and the partial formation of more soluble byproducts led to a second experimental activity in which NTP was applied as a pre-treatment to a laboratory-scale biofilter. Indeed, the efficiency of biological APC systems can be unsatisfactory when treating compounds that are lowly soluble in water. Thus, a mixture of air and five VOCs (toluene, *n*-heptane, *p*-xylene and the carcinogenic benzene and ethylbenzene) was selected to represent the air stripped from an industrial WWTP and the presence of more soluble compounds formed during the NTP treatment was confirmed by this second experimental activity. In addition to the issues related to compounds with low solubility, biotechnologies applied to APC suffer from unsteady conditions of flow rate and pollutant concentrations. Therefore, peaks of VOC inlet loading rate were simulated in the laboratory flow to understand if NTP was capable of taking charge of critical conditions for the proper operation of a biofilter. The pre-treatment operated by NTP effectively acted on abating the peak concentration of the five VOCs, including the carcinogenic compounds, prior to entering the biofilter. In conclusion, NTP showed encouraging results as a pre-treatment device supporting biofiltration in conditions of unsteady VOC inlet loading rate, which biofilters are often subject to in real cases.

7.2 Outlook

It is hoped that some of the integrative methodologies for exposure assessment and environmental monitoring will raise the interest of local environmental protection agencies, as in the case of sewage sludge sampling for the detection of anomalous situations of exposure to dioxin. Similarly, deposition monitoring coupled with the methodology to obtain the acceptable deposition of dioxin in several countries would help keeping the diet under control and prevent diet contamination. The introduction of a deposition limit value for PCDD/Fs is a necessary step towards this goal. Anyway, additional efforts should be made to improve the food traceability for a more accurate evaluation of the safety of each product.

In addition to prevent exposure, this doctoral research proposes technical solutions to prevent emissions. The most immediate and viable solution consists in replacing conventional biofilters with BTFs; this would allow improving the dispersion of the effluent in the atmosphere and reducing the local impacts; in addition, due to their more compact size and modularity, BTFs would be more convenient for public and private companies in terms of space required and in view of future enlargements of the facilities. Unfortunately, all biological technologies suffer from unsteady conditions of inlet loading rate, but a pre-treatment with NTP would solve this issue. However, additional research is needed to estimate the energy consumption of NTP at larger (pilot or real) scale and, if necessary, reduce the energy request. In the particular case of unsteady loads of pollutants, an improved energy efficiency should be pursued without considering the adoption of adsorbents or catalyst beds, since desorption of the pollutants trapped may occur in case of a decrease in the pollutant *ML*. The problem of energy efficiency is currently under investigation as part of a new project, recently started at the University of Trento. After an optimization of the energy consumption and costs, NTP would be ready to be proposed as an intermittent device that activates after incoming peaks of inlet loading rate detected by a flowmeter and a gas sensor (FID, FTIR or electrochemical sensors), to prevent stress to the microorganisms in a biological APC system; if unsteady conditions are limited or absent, NTP could be also adopted as a mobile device to be activated during the start-up phase of a biological APC system, in order to speed up this phase (as a pre-treatment) and/or to treat part of the flow, given the low efficiencies of biological technologies during this phase. In parallel, a research on photocatalysis with ultra-violet light is planned for the incoming months in view of potential applications as an alternative pre-treatment method in combination with biofiltration systems.

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