Client Ricerca di Sistema

Subject **EMISSION FACTORS OF DOMESTIC AND CENTRALIZED BOILERS: PRELIMINARY RESULTS**

Order

Notes Report for EGTEI (UN-ECE Expert Group on Techno-Economic Issues).
Based on A5028867 "Risultati preliminari delle prove di valutazione dei fattori di emissione da caldaie domestiche e centralizzate."

N. of pages 21 **N. of pages annexed** -

Issue date 20/08/2007

Prepared

Verified

Approved

Mod. RAPP v. 01

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REVISIONS HISTORY

Revision number	Date	Protocol	List of modifications and/or modified paragraphs
0	20/08/2007	A7022820	First emission

1 SUMMARY

This report describes the activities carried out in the framework of the GAME Project, especially regarding the assessment of emission factors, in domestic and centralised boilers.
After a preliminary classification of the domestic boilers based upon power, fuel and implemented technologies, the boiler models representing the whole set of boilers installed on the national territory were identified and tested to evaluate the emission factors.
In the same way, centralised boilers were categorised by fuel and technology, starting from the classic models up to the most advanced ones, in compliance with the environment constraints. For the selected boilers, a test plan has been elaborated, in order to supply a scenario as much as exhaustive of the species and emissions of pollutants.
The sampling methodologies adopted are also reported, as well as the complete list of the tests carried out and the preliminary results concerning conventional macro-pollutants, metals and anions and cations.

2 INTRODUCTION

The aim of the GAME Project is to identify the opportunities of application of the co-generation medium size (electricity + remote heating/cooling) plants in the city areas by an integrated technological, economical, environmental and social approach. This permit to avoid the "barriers" which often exist in the monothematic projects and to verify the use of validated methodological instruments and models.

From the environmental point of view, one of the main advantages associated to the development of the remote heating consists in the decreasing of the number of boilers for residential use. The project aims also to quantify the reduction of the total emissions in the atmosphere by the application of a "Receptor Model". In this context the knowledge of the boiler emission factors, for both conventional pollutants and micro pollutants is necessary.

The following goals are proposed:

- Implementation of an emission factor database of residential boilers under examination in the town of Piacenza (experience that can be replicated in other cities);
- Verification, on the field, of the appropriateness of the "Receptor Model", as instrument for the quick evaluation of environmental benefits, coming from the development of the remote heating technology.

In this report, the activities carried out and the analytical results available are shown.

3 SMALL BOILER CLASSIFICATION

The study of the emission factors was organised on the basis of the boilers installed on the local territory. The whole set was categorised in two sub-set of boilers: the first with a thermal power below 35 kW, and the second with a thermal power above 35 kW. The first is related to boilers that do not need any external manager, according the current Italian law, the second is related to boilers that need a third independent manager, different from the user and the installer.
In order to get representative emission factors, a preliminary step has consisted in identifying the boiler models which better characterise the local and the national situation. In this perspective a market survey was carried out with the aim to characterise the existing boiler types according to the thermal power, the technology and the fuel used.

3.1 Boilers with thermal power below 35 kW

This type of boilers is commonly defined as “domestic boiler”. It has the function of both home heating and sanitary water heating.

As far as this power size is concerned, the data collected in literature and available in a previous study, carried out by the Polytechnic University of Milan, were integrated with the survey on the boilers installed in Piacenza and in its province area. Using the information available from the main retailers we found out that the nominal power, for the single domestic boilers, ranges between 23 kW and 34 kW. The higher power size is typical of the last generation of boilers, having the double function of building heating and sanitary water heating. This is the reason why we defined 35 kW as the limit for our classification.

Methane is the most common fuel since it brings together management advantages and positive aspects related with the combustion and consequent emissions. In addition, methane is usually preferred to other fuels because the combustion is easy controllable through the main parameters such as the air/fuel ratio and the flame temperature. Only in a few applications, oil is still used: in particular where the plant modifications would turn out disadvantageous for a series of reasons related to the plant configuration and the boiler operating mode.

The implemented technologies are continuously evolving. The reason for the continuous development of the boiler combustion and thermal exchange technologies is mainly due to the need of reducing the fuel consumption, pursuing both the increase of the boiler efficiency and the reduction of the pollutant emissions. The latter aspect is characterised by the issue of more and more restrictive law directives, with the final objective of limiting the amounts of harmful substances released by the plants in the air. In terms of emission, nitrogen oxides (NOx) and carbon monoxide (CO) are among the most dangerous. While NOx are formed at high temperature and at high excess air values, CO is originated by incomplete combustion, when the oxygen in the combustion is insufficient to completely oxidise the carbon in the fuel. Therefore, on one side a reduction of the temperature peaks and the excess of air in the combustion area is pursued in order to hamper the NOx formation. On the other side a too low air/fuel ratio would compromise the combustion efficiency causing high CO levels in the flue gases. New developed technologies were went to try to find a compromise between these two opposite needs. Flat-flamed burners and flat bed burners characterised by low flames and lower temperatures with respect the classic burners, were developed in order to reduce the residence time of the combustion products in the warmer zone, therefore limiting the nitrogen oxides production. In the new developed total premix burners, gas and air are homogeneously mixed to provide a more uniform combustion, both spatially and in temperature profile. Other techniques, suitable to reduce the flame temperature, consist in the introduction of cooling active and passive elements in the proximity of the flame and in increasing the

heat dissipation in the concerned zone. This is realised through the means of small diameter tubes with cool water inside or ceramic elements for heat dissipation.
For what concerns the condensing boilers, they are the latest technological innovation available on the market, and they are gaining an increasing share in the national panorama. This type of boilers is characterised by high efficiency, even higher than 100%, since the water steam condensation heat in the flue gases is also exploited, having therefore the flue gas temperature around 40 °C, significantly lower than in the conventional case. At equal output power, the recovery of the condensation heat, otherwise lost in the flue gases, allows fuel savings even higher than 20%. The consequent saving of operating costs is partially offset by the higher investment cost of the plant, due to the larger heat exchanger (which allows the recovery of the condensation heat) and to the more complex structure, with respect to the conventional type.

Nowadays, another important technological issue to be considered in the management of the domestic boilers, is related with the modulation, which means the possibility to change the load following the power demand. Recently, more and more innovative systems have been developed allowing the achievement of high efficiencies at low load factors and providing quick availability in terms of sanitary hot water and heat. One of the systems consists in splitting the gas-feeding channel in two separated pipes, which alternatively feed the nozzles. Closing one of the two pipes, only a half of the nozzles are fed, therefore reducing the load factor.

One of the most meaningful categorisation, also reported in the regulations, is based upon the method of feeding the combustion air into the combustion chamber. Boilers where air is fed into the combustion chamber at atmospheric pressure are defined as “open air boilers” or “natural draft” (type B, UNI EN 297 regulation).
Otherwise, in boilers with “room-sealed” or “forced draft” (type C, UNI EN 483 regulation) the combustion air is moved by an appropriate fan and all the combustion components (nozzles, air and fuel pipes and the combustion chamber) remain isolated from the outside area in a safer and easier controllable way.
The boilers of the first category were mainly installed in the past. With the technology progressing, they were replaced by the “room-sealed” boilers, which are nowadays used in the most of the systems installed on the territory.
These boilers are characterised by lower heat dispersion and, therefore, the efficiency is approximately 1% higher. Moreover, these plants are considered safer, since the combustion zone is completely isolated from the area where the boiler is installed.

On the basis of the considerations made above, a sufficiently detailed scenario of the types of domestic boilers installed and their operating characteristics is depicted. The most representative models of boilers on the Italian territory are identified and selected to be analysed in laboratory tests to finally build the related emission factors database.
The survey carried out till now resulted in the selection of three main types of boilers:

1. “Open air boilers” or “natural draft” boilers, in which the combustion air flows into the combustion chamber at atmospheric pressure, with conventional burner. The old boilers for house heating fall in this category and they are approximately 20% of the total installed boilers.
2. “Room-sealed” or “forced draft” boilers, equipped with a fan usually located upstream the combustion chamber, which drives the combustion air into the combustion chamber from outside. These boilers are now the 80% of the total installed boilers, in Italy. According to information from the boiler manufacturers and installers, these boilers are equipped with a total premix burner that, as said above, provides a better combustion with reduced carbon monoxide emissions.
3. “Room-sealed” and condensation boilers, that have total premix burners. This category is one of the most common in some European markets, like The Netherlands; in Italy, this category accounts for approximately a 5% share of the total. It is envisaged that this category will increase the market share as well as the share of the total installations in the national scenario. The progress of the technology and the progressive reduction of the installation costs should make these boilers more and more profitable, due to, as mentioned before, remarkable savings both in terms of fuel and operating costs.

In 2003, the ATIG Association has carried out a survey at national scale aimed at the characterisation of the domestic boilers for building heating and sanitary water heating at national level. The results of this study are reported in the following tables.

Old or traditional boilers		new generation boilers		
92%		4%	4%	by ATIG
90%		5%	5%	by Assotermica
free circulation boilers	forced circulation boilers	Hi Technology boilers	condensation boilers	
23%	77%			

combined washing & heating			
for instant hot water	with hot water storage	only heating	
82%	12%	6%	by ATIG
88%	10%	2%	by Assotermica

The great majority of boilers (77%) are "room-sealed boilers" and "force draft" by a fan to control the combustion air entering the combustion chamber. The great majority of the boilers are combined boilers that means used both for simultaneous space heating and the sanitary water heating. The instantaneous boilers are widely prevailing, while only a fraction of approximately 10% has heat storage devices.

In terms of distribution and renewal we can notice the following situation:

	Single boiler installation	Fuelled by		
		natural gas	LPG/other	diesel
installed	14 million	75%	13%	12%
annual sales	1.2 million	80%	15%	5%

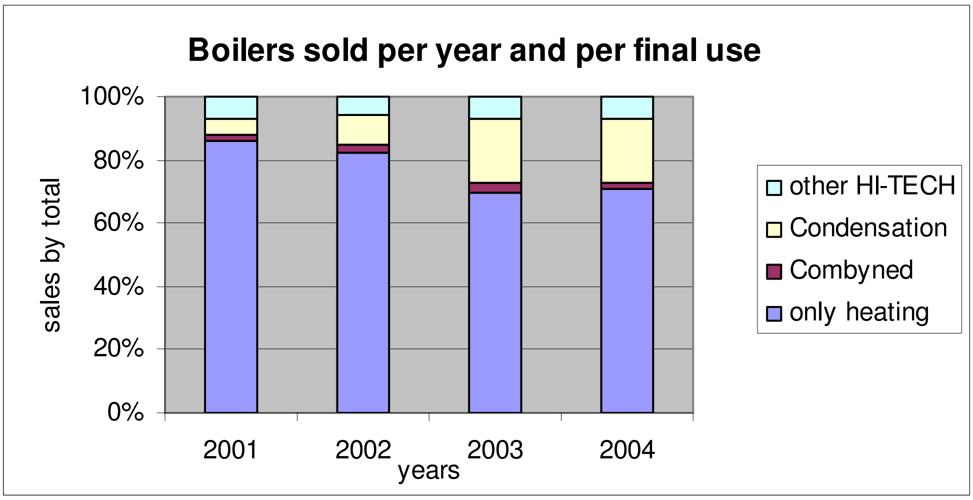
3.2 Boilers with thermal power above 35 kW

These boilers are generally called "collective domestic boilers" or "centralised plant" and are installed in residential or in public buildings such as offices, sport installations, school. On the basis of the Italian current legislation, an external manager different by the installer is required in order to guarantee a correct maintenance and management of the plant itself.
The fuel is the main characteristic that differentiates this type of boilers. In this higher range of power, boilers can be basically categorised as *liquid fuel boilers* and *natural gas boilers*. The natural gas boilers are approximately the 60% of the all boilers currently installed in Italy.

	residential centralised boilers	commercial centralised boilers	Fuelled by natural gas
installed	350'000	700'000	60%
annual sales	44'000		

Data on centralised boilers coming from Assotermica, (Association of the main Italian boiler

manufacturers) agree with the survey carried out by ATIG. They show the decreasing in the sales of open air boilers (from 7,6 to 6,2 thousand of units in the last 4 years) and a consolidation in sales of “room-sealed boilers” (approximately 15.000 units sold per year, since 2001).
For what concerns the distribution of the boilers on the national territory, the boilers can be categorised according their final use: building heating only or combined building heating + hot sanitary water production. With respect to the technological aspects, the boiler scenario is quite stable, with predominant preference for forced air boilers (beyond 80%). In the last biennium the sales of the condensation boilers increased quickly thanks to the fast spreading of this innovative technology, mainly due to the advantages of easier management and fuel savings. However, such technology is still a market niche share of the total number of high power boilers, notwithstanding the increased sales.
In the table below, the trend of sales is reported according to their final use. In absolute values, the total number of boilers, sold per year, remains constantly around 40000 units.



The observed increase in percentage for sales of condensation boilers is due to the spreading of this new technology. The other High Technology boilers have a stable trend even if they are continuously developed and the results, in terms of efficiency and emission reductions are improving more and more.

4 PLAN OF EXPERIMENTAL SURVEY

On the basis of the survey, a plan of sampling was established on field for centralised boilers and in laboratory for the small single units.
Consistently with the practical limits, a number of boilers deemed as representative of all the boilers operating at national level were selected with the aim of extending the results to a wider scenario. For each boiler under analysis a sample of the flue gases has been analysed in laboratory in order to estimate the emission factors for micro pollutants: heavy Metals, Polynuclear Aromatic Hydrocarbons (PAH), Volatile Organic compounds (VOC), Paraffin (linear and branched alkanes), Aldehydes, and Acetic acid. All these compounds allow us to define a real source profile that can be used in the application of the "Receptor Model".

A different approach is used for the two categories of boiler defined before: below and above 35 kW.
For the first one, since the tests are made in laboratory, an evaluation of the differences between specific models can be obtained. For the second one, for which field measurements are performed, an evaluation of the differences between liquid fuel (oil, diesel and biodiesel) can be obtained.

4.1 Sampling Methods

For all the boiler types the monitoring of flue gases, at the end of pipe, was carried out in two ways:

- Direct measurement of conventional or macro pollutants;
- Sampling on appropriate matrices and following laboratory analysis for non-conventional pollutants and micro-pollutants.

Both in direct measurement and in the sampling mode, the temperature of the flue gas at the end of pipe were measured.
In order to better simulate the real operating conditions of the boilers, reduced heat loads were taken into due account (in real operating adapting the output power to the demand) by manual load change. In the cases where the load cannot be modulated, series of on/off switching were operated, with consequent peaks of emissions being taken into account.
So the direct measurements were carried out in steady state combustion conditions (where possible), while samplings were carried out both in continuous mode (C), and in discontinuous mode (I - "intermittent") activating the switching on/off of the burners. This latter mode of sampling (discontinuous) was not applied to all the boilers, but simply on one boiler for each fuel type.
The conventional pollutants measured are CO_2, CO, SO_2, NO, NO_2, NOx, along with O_2.
The list of non-conventional pollutants measured is shown in the schema below.
Metals, anions and carbon were measured in the sample of total particulate matter.

Non Conventional pollutants and Micropollutants

Category	Chemical species
PAH (in solid and gaseous phase)	Naphthalene; 2-methyl-Naphthalene; 1-methyl-Naphthalene; 1,1-Biphenyl; 2,6-dimethyl-Naphthalene; Acenaphtylene; Acenaphthene; 2,3,5-trimethyl-Naphthalene; Fluorene; Phenanthrene, Anthracene; 1-methil-Phenanthrene; Fluoranthene; Pyrene; Benzo(a)Anthracene; Crysene; Benzo(b) Fluoranthene; Benzo(k) Fluoranthene; Benzo(e)Pyrene; Benzo(a)Pyrene; Perilene; Indeno(1,2,3-cd)Pyrene; Dibenzo(a,h)Anthracene; Benzo(g,h,i)Perilene.
Paraffins (in solid and gaseous phase)	n-C12; n-C13; n-C14; n-C15; n-C16; n-C17; Prystane; n-C18; Phytane, n-C19; n-C20; n-C21; n-C22; n-C23; n-C24; n-C25; n-C26; n-C27; n-C28; n-C29; n-C30; n-C31; n-C32; n-C33; n-C34; n-C35; n-C36; n-C37; n-C38; n-C39; n-C40.

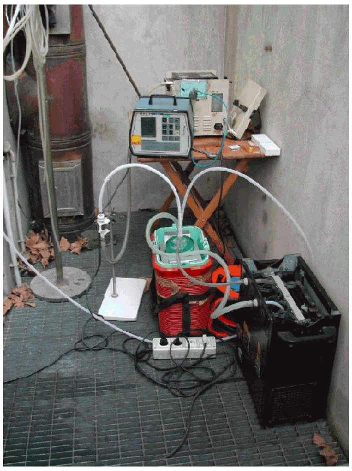
Category	**Chemical species**
Heavy metals on the particulate	Be; Al; Ti; Cr; Mn; Co; Ni; Cu; Zn; As; Se; Rh; Pd; Cd; Sn; Sb; Te; Ba; Pt; Tl; Pb; V; Ca; Mg; Na, K, Fe.
Anions - Cations on the particulate	SO_4, NO_3; NH_4.
Carbon on the particulate	Total Carbon
Alkanes and Alkens	n-Hexane (C6), n-heptane (C7), n-octane (C8), n-nonane (C9), n-decane (C10), n-undecane (C11), n-dodecane (C12), n-tridecane (C13), n-tetradecane (C14), 1-hexene (C6), 1- heptene (C7), 1-octene (C8), 1-nonene (C9), 1-decene (C10), 1-dodecene, 1-tetradecene, *cis* 2-hexene , *trans* 2-hexene, *trans* 2-heptene, *trans* 2-heptene, *cis* 3-heptene, *trans* 3-heptene, 4-methyl-1-pentene, 4-methyl-2-pentene, 2-methyl-1-pentene, 3-etylbenzene, 4-etylbenzene, 2-etylbenzene, 1,2,3-trimethylbenzene.
Aldehydes	Formaldehyde, Acetaldehyde; Acrolein; Acetone; Propionaldehyde; Crotonaldehyde; Butyraldehyde; Benzaldehyde; Isovaleraldehyde; Valeraldehyde; o-Tolualdehyde; m-Tolualdehyde; p-Tolualdehyde; Hxaldehyde; 2,5-Dimethylbenzaldehyde.
VOC aromatics	Benzene, Toluene, Monochlorobenzene, Ethylbenzene, m+p-Xylene, Styrene, o-Xylene, Isopropylbenzene, Bromobenzene, n-Propylbenzene, 2-Chlorotoluene, 4-Chlorotoluene, 1,3,5-Trimethylbenzene, ter-Buthylbenzene, 1,2,4-Trimetilbenzene, sec-Buthylbenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, p-Cymene, 1,2-Dichlorobenzene, n-Butylbenzene, 1,2,4-Trichlorobenzene, Naphthalene, 1,2,3-Trichlorobenzene, 1,3,5-Trichlorobenzene, Bromochloromethane, Dibromomethane, Bromodichloromethane, Dibromochloromethane, 1,2-Dibromoethane, Tribromomethane, 1,2-Dibromo-3-chloropropane, 1,1-Dichloroethene, Dichloromethane, *trans* Dichloroethene, 1,1-Dichloroethane, *cis* 1,2-Dichloroethene, Trichloromethane, 1,1,1-Trichloroethane, 1,2-Dichloroethane, 1,2-Dichloropropene, Carbon Tetrachloride, Trichloroethylene, 1,2-Dichloropropane, *cis* 1,3-Dichloropropene, 1,1,2-Trichloroethane, 1,3-Dichloropropane, Tetrachloroethene, 1,1,1,2-Tetrachloroethane, 1,1,2,2-Tetrachloroethane, 1,2,3-Trichloropropane, Hexachlorobutadiene, Trichlorofluoromethane.
Acetic Acid	Acetic Acid

The sampling methods and the analytical ones are the followings:

Pollutants	**Measurement/sampling Method**	**Analytical Method**
Conventional (CO_2, CO, SO_2, NO, NO_2, NOx, O_2)	Multiparametric analyser with electrochemical cells with heated line	-
PAH e Paraffin	Samplings on quartz fiber filter for the particulate phase; adsorbing resin XAD2 for the non-condensable phase, water vapour collector. Flux of 10 l/min, duration of 100 min.	EPA 3510 (extraction), EPA 8270 (analysis by HRGC/LRMS).
Heavy metals on the particulate	Samplings on quartz fiber filter with heated line. Flux of 15 l/min duration of 100 min..	ASTM D5673/02 after acidic digestion
Anions and Cations on the particulate		Anions: ISO 10304. Cations: ISO 14911 after extraction with aqueous solution
Carbon on the particulate		Internal Method

VOC aromatics Alkanes Alkenes	Samplings on vial of active carbon with condense separator before. Flux of 0.2 l/min duration of 25 min.	EPA TO 17
Aldheydes	Samplings on acid solution of 2,4-Dinitrodiphenylhydrazine according to the US EPA method 0011 "Sampling for selected aldheyde and ketone emissions from stationary sources". Flux of 1 l/min duration of 100 min.	EPA 8315 (for the extraction and for the analysis by HPLC)
Acetic Acid	Samplings by 5% Na_2CO_3 on Chromosorb P with condense separator before. Flux of 0.5 l/min duration of 100 min.	Internal Method

Some photos of the sampling apparatus are shown below.



The apparatus consists in a nozzle, through which the flue gas sample is taken, then flowing into condenser system (cooling system) where the condensable part is separated to avoid any damage to the following filtering and storage system. Then the flue gases are filtered and collected in proper containers (vials), after the suction pump and the volumetric meter. The sampling vials and filters are then analysed in laboratory, as well as the residual substances coming from the condensation and watering processes.

4.2 Tests on individual domestic boilers (Pt<35 kW)

For what concerns the single unit house boilers, the laboratory tests involved four boiler types, with different characteristics representative of the whole set of boilers operating at national level.

1) Boiler Saunier Duval model "Themaclassic C 25 E" :
   free circulation boiler with conventional burner without air modulation system.
2) Boiler Immergas model "Eolo Eco":
   forced circulation boiler with premix burner (low NOx) (class 5 of NOx emission classes)
3) Boiler Unical model "ALKON35C":
   forced circulation boiler with premix burner and flue gas condensation
4) Boiler Unical model "EVE CTFS":
   forced circulation boiler with conventional burner without air modulation system. ***Used and stressed boiler to evaluate long time response***.

Test are performed in the laboratory and the sampling program is related to the evaluation of the different operating regimes, namely, at full thermal load, at minimum thermal load, at on/off switch mode timer controlled, and in transient conditions, manually operated in continuous mode. The differentiation of the above conditions had the objective of simulating the “real” operating conditions as much as possible.

4.3 Tests on collective domestic boilers (Pt>35 kW)

In the following table, the schema of substances emitted and tested in laboratory is reported in relation to the boiler types tested in this work.
The tests were carried out at different operating regimes, namely, at full thermal load, and in transient conditions with on/off switches operated manually during continuous mode. The variability of the above conditions had the objective of simulating the “real” operating conditions, as much as possible.
For what concerns the operation mode, “C” indicates continuous running regime, while “I” indicates intermittent running tests.

Fuel	type of boiler or its use	working conditions during tests	number of tested boilers		gas	particulate matter	heavy metals	anions & cations	carbon	IPA & parafines	aldeydes	acetic acid	aromatic VOC
			< 500 kW	>500kW									
natural gas	heating	C + I	5	1	X	-	-	-	-	X	X	X	X
	combined (washing & heating)	C	1	0	X	-	-	-	-	X	X	X	X
	With flue gas condensation	C	1	0	X	-	-	-	-	X	X	X	X
	premix with air modulation system	C	2	2	X	-	-	-	-	X	X	X	X
Diesel	heating	C + I	2	0	X	X	X	X	X	X	X	X	X
Bio-diesel	heating	C + I	3	0	X	X	X	X	X	X	X	X	X
Oil	heating	C + I	0	2	X	X	X	X	X	X	X	X	X
	premix with air modulation system	C	0	2	X	X	X	X	X	X	X	X	X

**C = continuous working   I = intermittent forced working*

The particulate matter samplings have not been carried out for the natural gas boilers because after the initial samplings, even in long time measurements, negligible concentrations of PM have been found. For each category a sufficient number of boilers were considered as sample representative of the whole boiler set at national level. In order to improve the representativeness of the study, both low and high power boilers (below and above 500 kW) were selected.
The sampling program were successful in testing different boilers, including a minimum of 1 boiler per each fuel, boiler size and technology. Moreover, in order to guarantee the completeness in the experimental results, duplicate tests were carried out for the most common boiler types. Small size oil boilers are missing in the sample simply because this boiler size is actually not installed in the domestic sector, while it is quite common as large boiler in the industrial sector where savings of raw material is predominantly searched.
Also large size biodiesel boilers are not included in the analysis since the biodiesel fuel is not common yet and, therefore, not yet used in large buildings or factories also due to the scarce availability of this fuel on the market.

5 PRELIMINARY RESULTS

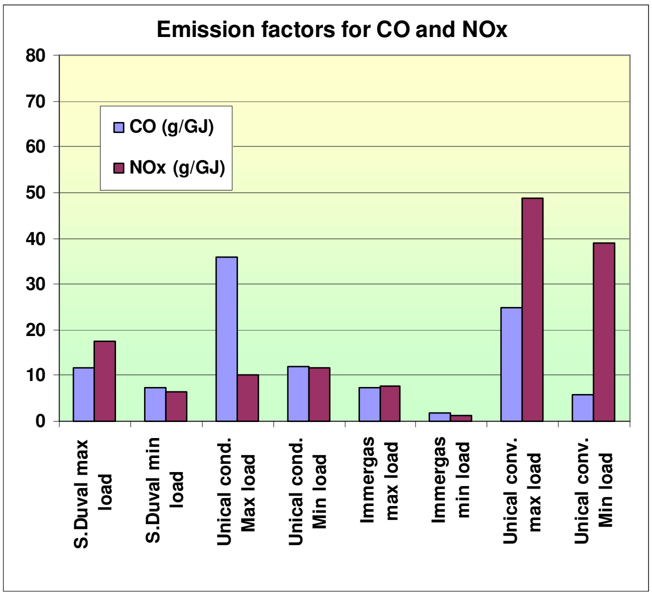
In the following tables, the available preliminary results concerning the measurements of conventional macro-pollutants, metals and anions and cations on the centralised boilers are reported.
All the results are presented as emission factors that can be classified in respect to the fuel and technical characteristic of boiler.
Starting from the boiler operating data and the measurement results, the emission factors have been elaborated through the "GASPRO" software developed by the Polytechnic University of Milan.
The "GASPRO" software starts from the composition of the fuel and the oxygen (%) in emissions, entered as input parameters and estimates the volume of the gas generated by the combustion process. This data, properly elaborated, leads to the estimation of the emission factors.
The available results are shown in graph and table form. Since the analysis of the liquid fuel is still in progress, the reported data are related to a "typical composition" and will be updated as soon as the experimental data will be available.

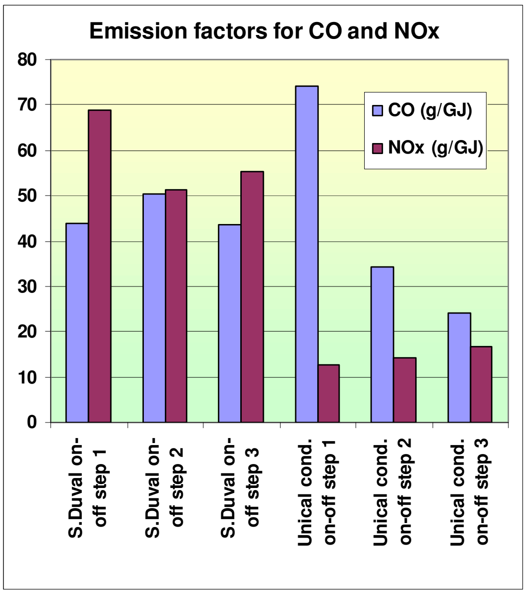
5.1 Individual domestic boilers (Pt<35 kW)

For what concerns the single unit house boilers, the laboratory test involved the four boiler types mentioned before:

- a UNICAL condensation boiler,
- a Saunier Duval (no modulation) open air boiler,
- an Immergas "room-sealed" boiler equipped with pre-mix burner,
- a UNICAL "room-sealed" boiler (already previously tested and therefore comparable with an "old" boiler).

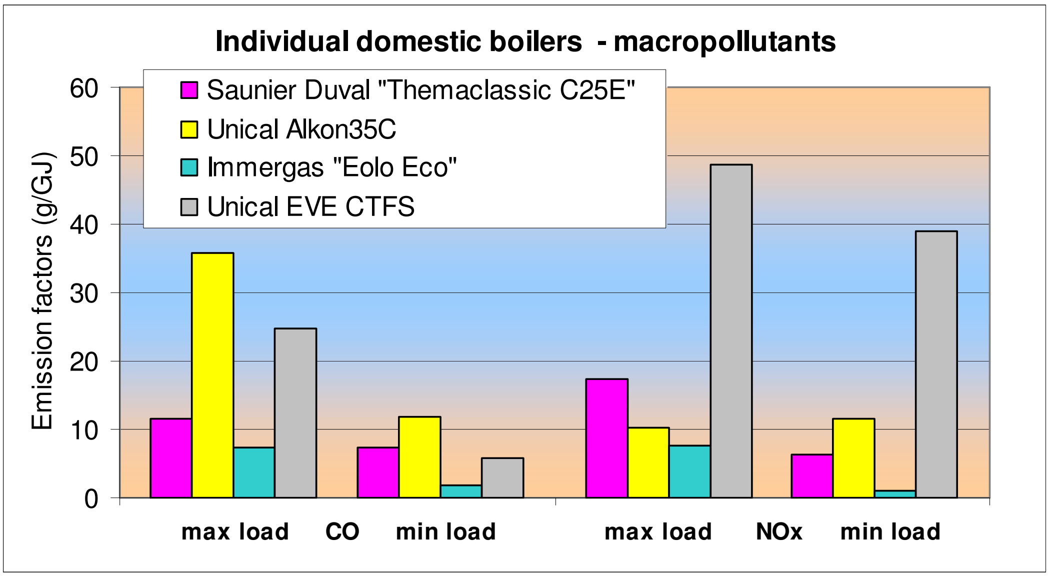
In the following, the results of the analysis on the test samples are reported.
Considering that the only fuel is natural gas, for macro or conventional pollutants the analysis is related only to CO and NOx.



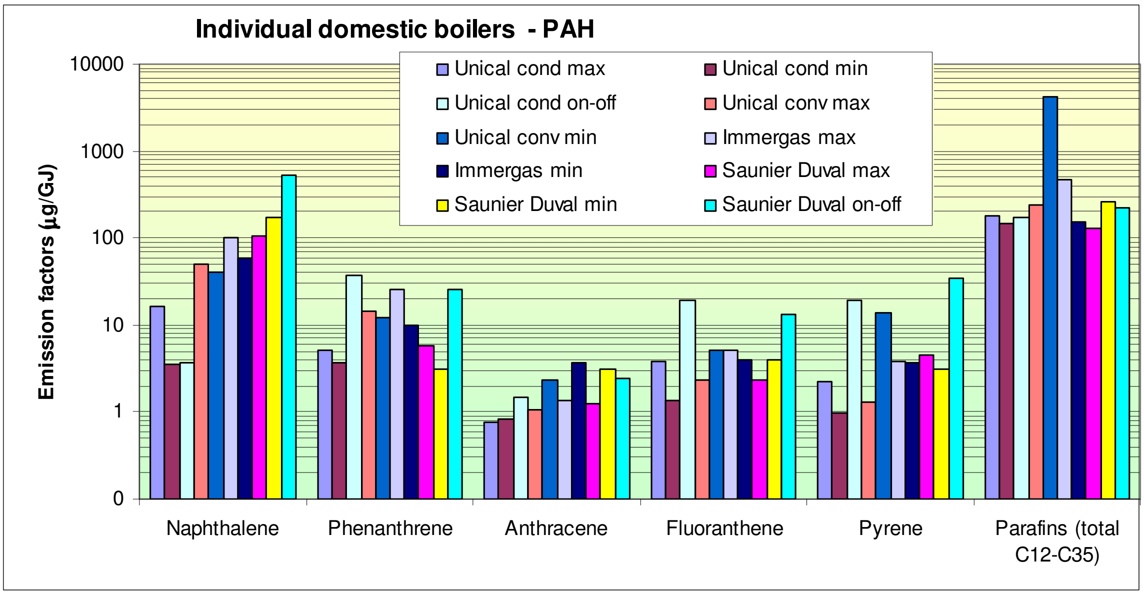


As shown in the figure, the UNICAL condensation boiler and the Immergas with pre-mix burner, which are the most technologically advanced models, provided the best performances also for what concerns the micro-pollutants emissions. The premix burner is efficiently reducing NOx emission also during

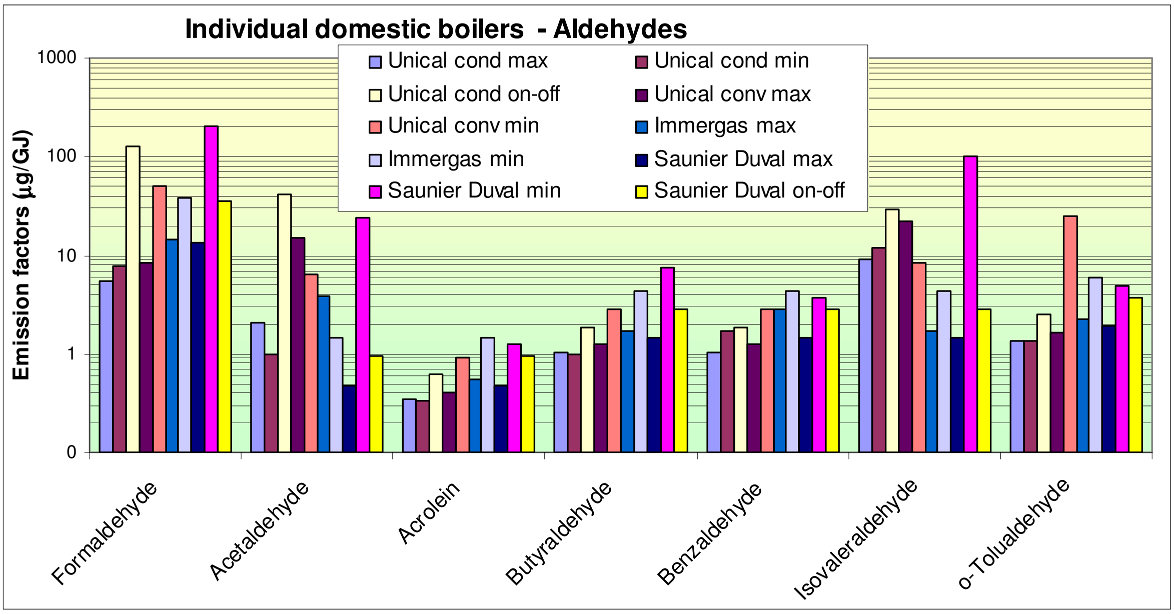
intermittent regime (1, 2 or 3 switch on/off). In particular the low values of NOx emissions rank these boilers in the most efficient class defined by the European regulation. Moreover, it is noted that peaks in the emission are observed in the intermittent operation mode for both the boilers sampled in these conditions.
Comparisons between the four boilers in the same sampling continuous mode conditions (minimum and maximum load) are shown in the following figure.



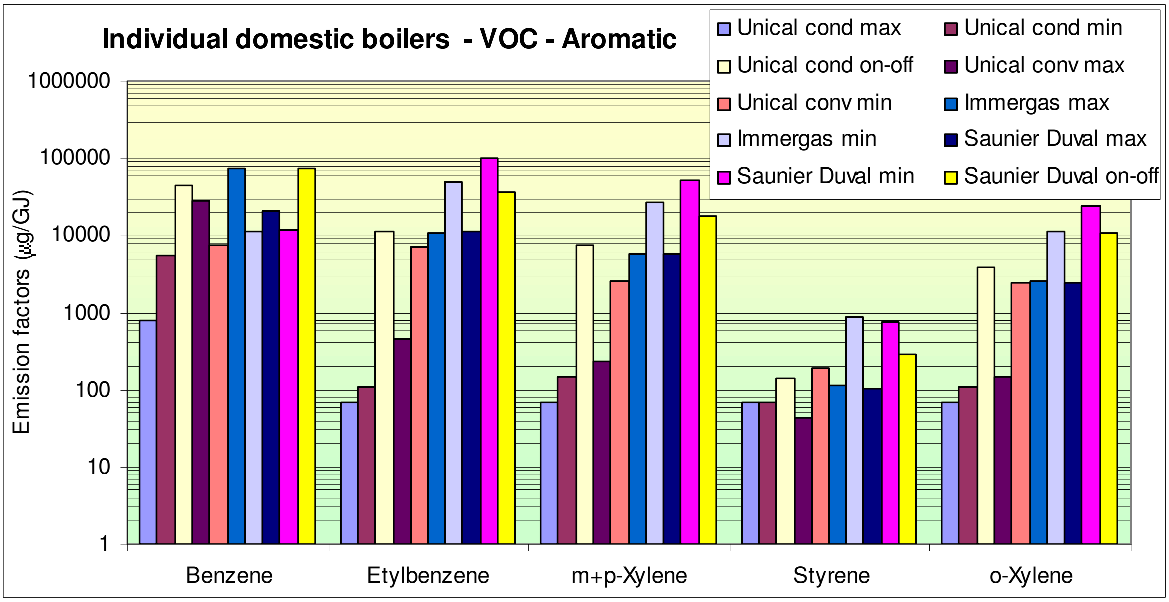
Also the PAH emission factors (following figure) show higher average values in the non-continuous operation mode, while under the same operating conditions the same emission factors are lower for boilers equipped with abatement emission devices, like the pre-mix Immergas boiler and the Unical condensation boiler. The naphthalene is the most significant comparison parameter since the other compounds show negligible values.



Similarly to the centralised boilers, also in the small single units peak values of aldehydes are found particularly for the Saunier Duval boiler working at minimum load. In the other cases the values are quite regular and limited in particular for the most technologically advanced models working in continuous mode.



For what concerns the Volatile Organic Compounds (VOC), including the aromatic compounds, the possible observations are similar to what already said for aldehydes. Benzene and xylenes are the most detected substances while other substances are negligible. Like for all the other pollutants, the continuous operating mode is characterised by a better emission profile especially for the most technologically advanced models.



The UNICAL condensation boiler and the IMMERGAS with pre-mix burner, which are the most technologically advanced models, provided the best performances for what concerns the micro-pollutants emissions.

5.2 Collective domestic boilers (Pt>35 kW)

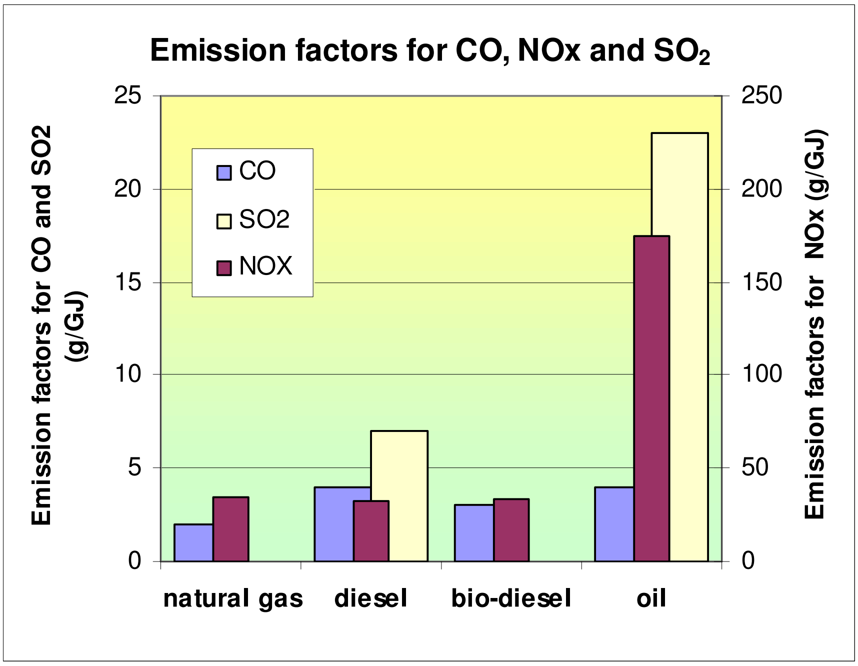
In the following table the values of concentration of conventional pollutants are shown as a function of fuel and boiler final use. In order to provide a synthetic comprehensive schema, the average values concerning all the tests performed are reported.

Fuel	type of boiler or its use	working conditions during tests	O2 (%)	CO2 (%)	CO (mg/Nm3)	SO2 (mg/Nm3)	NOx (mg/Nm3)	TSP (mg/Nm3)
natural gas	heating	C + I	8.1	7.4	3.7	0.0	86.1	-
	combined (washing & heating)	C	2.8	10.6	< 0.01	0.0	129	-
	With flue gas condensation	C	12.2	5.5	16.2	0.0	12.3	-
	premix with air modulation system	C	10.8	6.4	39.4	0.0	56.4	-
Diesel	heating	C + I	9.0	8.6	12.5	18.6	81.0	3.6
Bio-diesel	heating	C + I	13.5	5.4	3.7	0.0	86.1	0.08
Oil	heating	C + I	4.1	12.4	15.6	80.1	618	46.1
	premix with air modulation system	C	10.2	8.4	21.9	15.6	238	28.0

**C = continuous working I = intermittent forced working*

The measurements of Particulate Matter for natural gas are not reported because after preliminary measurements it came out that the detected amount was negligible.
CO values are lower in the boilers operating in combined mode and, as expected, NOx emissions are definitely limited in the condensation boilers**.**

The estimation of the emission factors is shown in the graph and the range of evaluations is reported in the following table. Since the analysis of the liquid fuel is not at disposal, the reported data are related to a “typical composition”.
Almost all the boilers tested are in class 3, an intermediate class, according to the categorisation of the boilers on the basis of their NOx emissions (directive UNI EN 483). Only the condensation boilers are considered consistent with the environment constraints, thanks to the innovative technology implemented.



Moreover, it is interesting to note the drastic decrease of SO2 and NOx emissions as the fuel changes from oil to diesel oil and, even better to biodiesel.

Fuel	type of boiler or its use	working conditions during tests	samples	CO	NOX	SO2
			nr	(g/GJ)	(g/GJ)	(g/GJ)
natural gas	heating	C + I	6	1 ÷ 2	30 ÷ 41	0
	combined (washing & heating)	C	1	0	37	0
	With flue gas condensation	C	1	10	7	0
	premix with air modulation system	C	4	1 ÷ 48	24 - 60	0
Diesel	heating	C + I	2	0 ÷ 7	23 ÷ 41	5 ÷ 9
Bio-diesel	heating	C + I	3	1 ÷ 5	30 ÷ 37	0 ÷ 1
Oil	heating	C + I	2	4 ÷ 5	167 ÷ 182	15 ÷ 31
	premix with air modulation system	C	2	1 ÷ 23	149 ÷ 154	< 12

In the following two tables are shown the concentrations of the metals collected during the measurement campaign and the emission factors evaluated with the GASPRO program.
The concentrations are reported for all the samplings carried out, that is for all the liquid fuel boilers and final use of the plant; the emission factors instead are ordered only per fuel of the boiler.

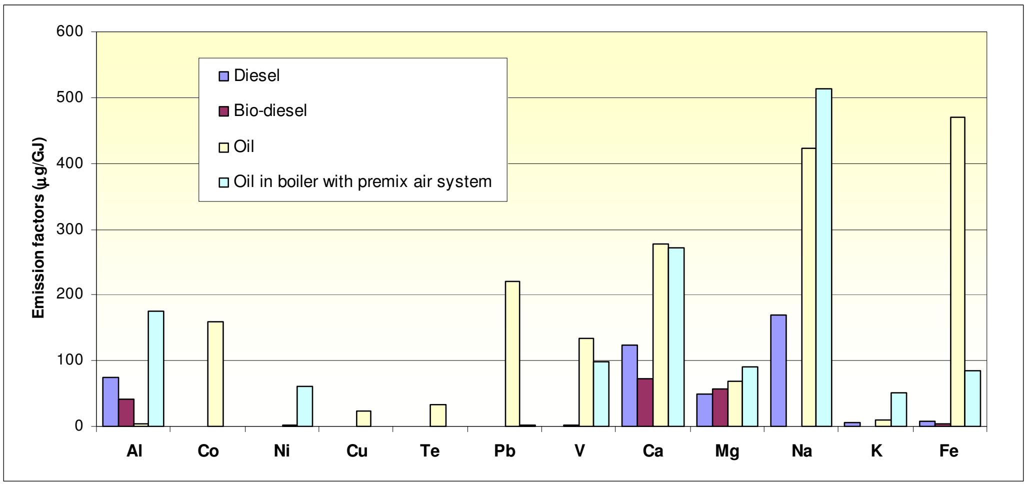
Heavy metal concentration in particulate matter ($\mu g/Nm^3$)												
Heavy Metals	Diesel only heating 1st	Diesel only heating 1st (intermittent running)	Diesel only heating 2nd	Biodiesel only heating	Biodiesel only heating 1st (intermittent running)	Biodiesel only heating 2nd	Biodiesel only heating 3rd	Oil only heating 1st	Oil only heating 1st (intermittent running)	Oil only heating 2nd	Oil High Technology 1st (average of 2 tests)	Oil High Technology 2nd
Be	0.02	0.03	<D.L.	0.02	0.02	0.04	0.01	0.05	0.05	0.06	<D.L.	<D.L.
Al	116	191	220	174	159	67.1	45.3	14.2	9.24	22.4	392	359
Ti	1.93	2.10	3.43	0.68	1.71	1.13	0.84	2.97	3.06	3.23	15.7	8.85
Cr	0.34	0.28	0.32	0.17	0.31	0.89	0.19	14.9	13.8	13.8	4.88	1.49
Mn	0.21	0.16	0.18	0.11	0.17	0.48	0.10	20.8	20.1	22.1	1.41	1.58
Co	0.01	0.01	0.01	0.01	0.01	0.02	0.01	634	597	496	0.74	1.44
Ni	0.16	0.09	0.36	0.06	0.13	0.59	0.11	6.11	4.67	5.61	96.8	151
Cu	0.47	0.27	0.35	0.43	0.47	4.47	0.88	126	56.0	71.7	0.65	1.18
Zn	0.63	0.44	0.38	0.25	0.20	0.83	0.45	1.94	1.89	1.99	5.50	10.4
As	0.09	0.04	<D.L.	0.05	0.03	<D.L.	<D.L.	1.59	1.89	2.77	0.10	0.23
Se	0.21	<D.L.	0.09	0.33	0.26	<D.L.	<D.L.	0.08	<D.L.	<D.L.	0.42	0.17
Rh	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	0.12	0.14	0.29	<D.L.	<D.L.
Pd	0.05	0.12	0.17	0.05	0.04	0.07	0.04	0.09	0.11	0.09	0.24	0.16
Cd	0.09	0.02	0.00	0.02	0.02	0.02	0.01	5.56	3.41	4.68	0.04	0.06
Sn	0.36	0.32	0.64	<D.L.	<D.L.	0.23	0.22	0.20	0.17	0.18	1.41	1.26
Sb	0.03	0.08	<D.L.	0.03	0.01	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	0.06
Te	0.00	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	117	126	118	<D.L.	<D.L.
Ba	15.6	8.89	16.6	7.37	7.77	7.74	5.40	<D.L.	<D.L.	<D.L.	27.0	24.6
Pt	0.04	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	0.11	0.10	0.08	<D.L.	<D.L.
Tl	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	<D.L.	27.4	22.6	25.9	<D.L.	<D.L.
Pb	0.17	0.09	0.11	0.07	0.07	0.12	0.07	861	802	713	2.33	4.38

Heavy metal concentration in particulate matter (µg/Nm³)												
Heavy Metals	Diesel only heating 1st	Diesel only heating 1st (intermittent running)	Diesel only heating 2nd	Biodiesel only heating	Biodiesel only heating 1st (intermittent running)	Biodiesel only heating 2nd	Biodiesel only heating 3rd	Oil only heating 1st	Oil only heating 1st (intermittent running)	Oil only heating 2nd	Oil High Technology 1st (average of 2 tests)	Oil High Technology 2nd
V	0.37	0.46	0.17	0.47	0.44	5.91	5.65	292	407	709	159	247
Ca	262	285	302	255	246	149	138	703	874	1365	587	572
Mg	104	115	110	103	96.3	276	207	140	213	378	199	187
Na	<D.L.	<D.L.	640	<D.L.	<D.L.	<D.L.	<D.L.	880	1344	2244	1131	1062
K	0.66	1.72	61.4	0.38	0.09	<D.L.	<D.L.	36.1	28.8	35.7	113	102
Fe	15.6	15.7	16.1	11.9	18.5	1.78	0.71	1650	1578	1810	131	213

The alkaline earth metals (Ca, Mg and Na) were detected in all the cases with the exception of Na for the biodiesel. Al is found in diesel fuel and biodiesel for heating use, while Al is quite reduced for fuel oil. In the fuel oil also Co, Cu, Te, Pb, V, and Fe were detected; they are partially reduced only in the new technology boilers (High Technology). In this latter category, however, high levels of Al, Ni and Ba, have been found.

Heavy metals	Diesel only heating [µg/GJ]	Biodiesel only heating [µg/GJ]	Oil only heating [µg/GJ]	Oil HI TECH [µg/GJ]
Be	0,01	0,01	0,01	<D.L.
Al	74,4	41,2	4,3	175,6
Ti	1,02	0,39	0,86	5,52
Cr	0,14	0,12	3,96	1,37
Mn	0,08	0,07	5,88	0,71
Co	0,00	0,00	160,2	0,54
Ni	0,08	0,06	1,53	60,4
Cu	0,16	0,44	23,5	0,45
Zn	0,23	0,14	0,54	3,9
As	0,03	0,02	0,59	0,08
Se	0,07	0,12	0,02	0,13
Rh	<D.L.	<D.L.	0,05	<D.L.
Pd	0,05	0,02	0,03	0,09
Cd	0,02	0,01	1,27	0,02
Sn	0,18	0,07	0,05	0,62
Sb	0,03	0,01	<D.L.	0,03
Te	0,00	<D.L.	33,6	<D.L.
Ba	5,9	2,5	<D.L.	12,1
Pt	0,02	<D.L.	0,03	<D.L.
Tl	<D.L.	<D.L.	7,08	<D.L.
Pb	0,06	0,03	220,7	1,66
V	0,16	1,03	133,4	98,9
Ca	124,6	72,2	277,8	272,4
Mg	48,9	57,2	69,4	90,4
Na	168,5	<D.L.	423,4	513,8
K	5,81	0,09	9,40	50,2
Fe	7,03	3,15	470,8	84,1

The figure shows a limited number of metals to point out the ones with higher values.



Similarly to the case of the macro-pollutants, even for metals, the biodiesel seems to be the best choice from the environmental point of view. For what concerns the effects of the different technologies, assumed the same fuel, the Hi-Tech fuel oil boilers provide limited iron, vanadium and lead emissions, compared to the conventional technology, although showing a small increase in potassium, sodium and aluminium emissions.

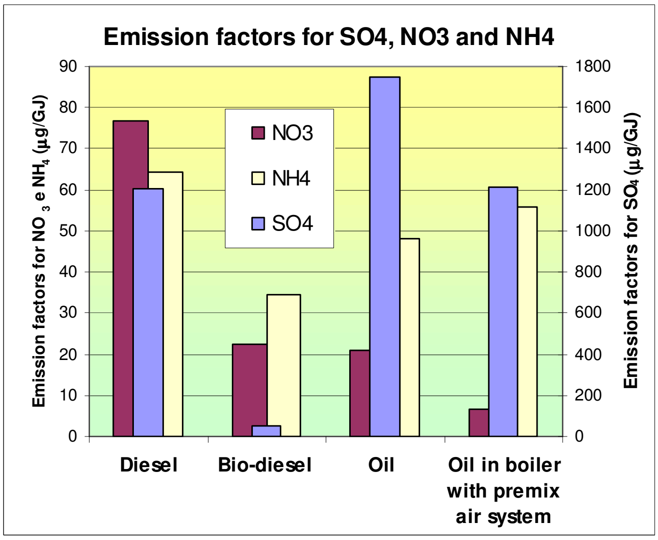
As made in the case of metals, the values of the anion and cations concentrations measured during the sampling campaigns are reported in the following.

Anions and Cations Concentration (µg/Nm^3)												
Anions and Cations	Diesel only heating 1st	Diesel only heating 1st (intermittent running)	Diesel only heating 2nd	Biodiesel only heating	Biodiesel only heating 1st (intermittent running)	Biodiesel only heating 2nd	Biodiesel only heating 3rd	Oil only heating 1st	Oil only heating 1st (intermittent running)	Oil only heating 2nd	Oil High Technology 1st (average of 2 tests)	Oil High Technology 2nd
SO4	1728	1432	107	185	263	56.6	34.7	5139	6797	6773	2135	2880
NO3	14.8	78.5	<D.L.	62.1	67.4	98.0	40.4	77.2	95.4	55.9	<D.L.	12.0
NH4	6.89	101	7.00	90.5	105	96.5	92.5	241	246	40.9	26.1	186

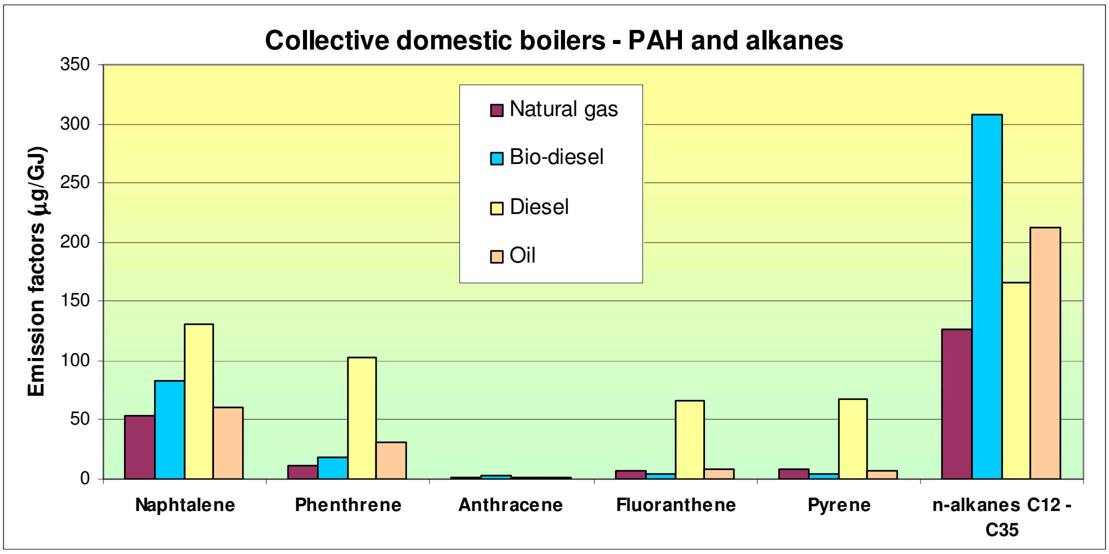
In the table below the estimated emission factors are shown, on the basis of the data collected for the anions and cations.

Sulphur and Nitrogen anions and cations emission factors ([µg/GJ]				
Anions Cations	Diesel only heating [µg/GJ]	Biodiesel only heating [µg/GJ]	Oil only heating [µg/GJ]	Oil HI TECH [µg/GJ]
SO4	1206,2	50,8	1748,8	1209,1
NO3	76,9	22,5	21,1	6,6
NH4	64,4	34,5	47,9	55,9

Generally very limited values are found for biodiesel fuel. Even for what concerns anions and cations concentrations detected in the particulate matter, the biodiesel seems to be the best fuel.
The sulphate values are significant in case of diesel oil boilers for heating use and in the high technology boilers burning fuel oil. The nitrates have the maximum value in case of diesel oil boilers for heating use and they are drastically reduced by the implementation of the new technologies. The ammonium nitrate remains practically constant.
Regarding the oil, the load modulation allows to significantly reduce the sulphates, while accepting a slight increase in the ammonia emissions.



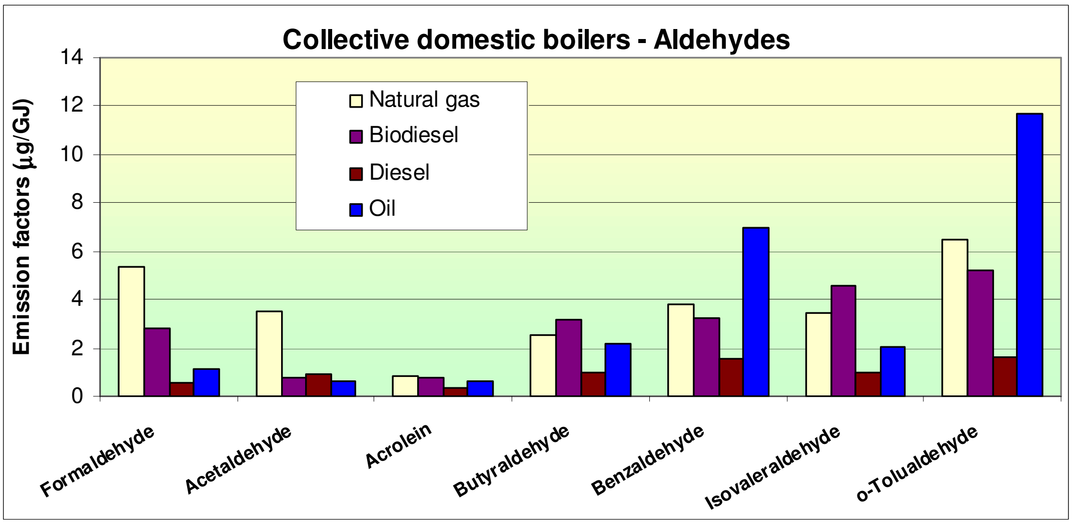
The emission factors for PAH and paraffins (following figure) show peaks in the case of diesel oil boilers; in the case of biodiesel, only the paraffins have significant values.



In specific transient operating conditions highest values are found in fuel oil boilers, especially for naphthalene and paraffins. It should be noted as even in biodiesel boilers higher values are found in transient operating conditions.

The aldehydes show quite equal values (following figure) still a little bit lower in the case of gas oil boilers, while the fuel oil boilers show higher values of benzaldehyde and O-tolualdeyde.

It should be noted that, for natural gas boilers in transient operating conditions, equipped with advanced technology (condensation or modulation), the emissions of formaldehyde and acetaldehyde are higher, while some peak of isovaleraldeyde are observed.



Looking at the Volatile Organic Compounds (VOC) and especially the aromatic compounds, a peak of trimethylbenzene is observed in fuel oil boilers and a peak of styrene for diesel and oil boilers. For what concerns the other substances, the values are found in the average, although noting lower emission factors in natural gas boilers, with respect the liquid fuel boilers. In transient operating conditions, in fuel oil boilers, the emissions significantly increase, in the most of the cases.