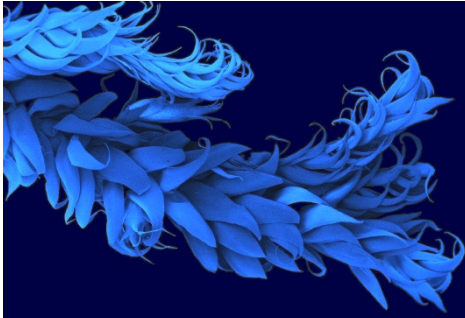


- Population is continuously increasing.
- The improvement of our life quality is linked to many disciplines (medicine, pharmacology, engineering: what we call «science and its products»), but also to the process of **industrialization of the production of goods**, agriculture included.
- In the modern world, the life quality is measured by the products we have at our disposal. We need more products, most of them produced at industrial level, and distributed worldwide: the production, commerce and movement of goods is fundamental for sustaining the economy at world level.
- The industrialization is based on the development of technology; technology needs new materials, provided by specific research fields such as chemistry and engineering; some of these new materials, with very special characteristics, are specifically designed to be harmful for some organisms, others are harmful if in the wrong place in the wrong time at the wrong concentration.
- All human activities need energy, whose production largely depends on burning processes. Also the movement of goods and people needs energy...
- Finally, important portions of what we produce or use in the production process, soon or later, will enter into the ecosystems, as lost fractions of the production process, as by-products of low value, or as waste at the end of the life of the good itself.



Plastic waste piles up on a beach off Panama City. LUIS ACOSTA/AFP/GETTY IMAGES





“Air pollution” is a term that indicates all physical (particulate), chemical and biological agents that modify the natural characteristics of the atmosphere.

A pollutant is a substance that determines the alteration of a stationary situation through:

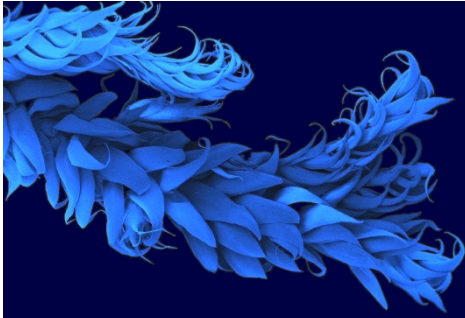
- Modification of physical and/or chemical parameters;
- Change in quantitative ratios of substances already present;
- deleterious effects on life (directly or indirectly).

Given the great variety of substances present in the atmosphere, numerous methods of classifying pollutants have been proposed:

- 1) based on the **physical state**: gaseous, liquid or solid;
- 2) based on the **chemical composition**, so we are mainly talking about compounds that contain sulphur, nitrogen, inorganic vs. organic carbon; halogen compounds.
- 3) based on the **genesis** and degree of reactivity in the atmosphere, in primary or secondary substances.

Primary: its release into the environment derives from its emission or production from the sector; carbon monoxide (CO) is an example of a primary pollutant, because it is a byproduct of combustion.

Secondary: production takes place in the sector itself or in the receiving environment, following transformations; the formation of ozone in smog is an example of a secondary pollutant.



Pollutants can arise from:

- natural sources
- anthropic (=human) activities.

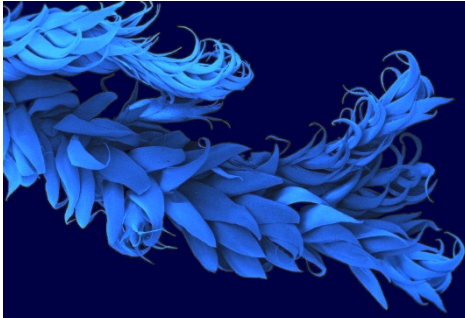
Among the first, the most important are:

- volcanic eruptions and geothermal release;
- microbial metabolism;
- marine aerosols;
- forest fires;
- gaseous release from vegetation (in particular organic hydrocarbons);
- dust dispersion;
- formation of O_3 (ozone) by lightnings.



With the exception of the first two manifestations, they are generally widespread across the territory, and their effects are not very intense, even if they remain important in the complex of biogeochemical cycle phenomena.





In contrast, anthropogenic sources are typically concentrated in urban and industrial areas.

On the basis of their characteristics, they can be distinguished into **instantaneous** vs. **continuous**.

On the basis of their topological distribution, they can be distinguished into:

LOCALIZED (or “punctiform“ or “point sources”), i.e. isolated sources, for which the dilution and dispersion of the effluents are such that the effects are normally limited to a radius of a few km.

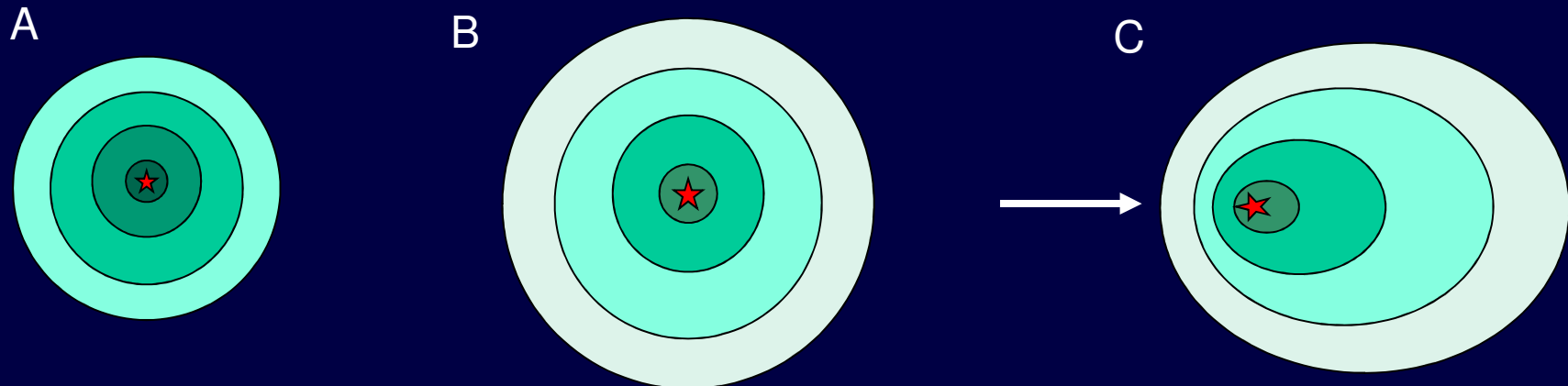
Point sources are the simplest to study, and can provide very interesting data on the modes of action of pollutants released into the environment, which can be investigated thanks to the clear concentration gradients that are formed due to dilution phenomena with respect to the emitting source.

Important factors to consider are:

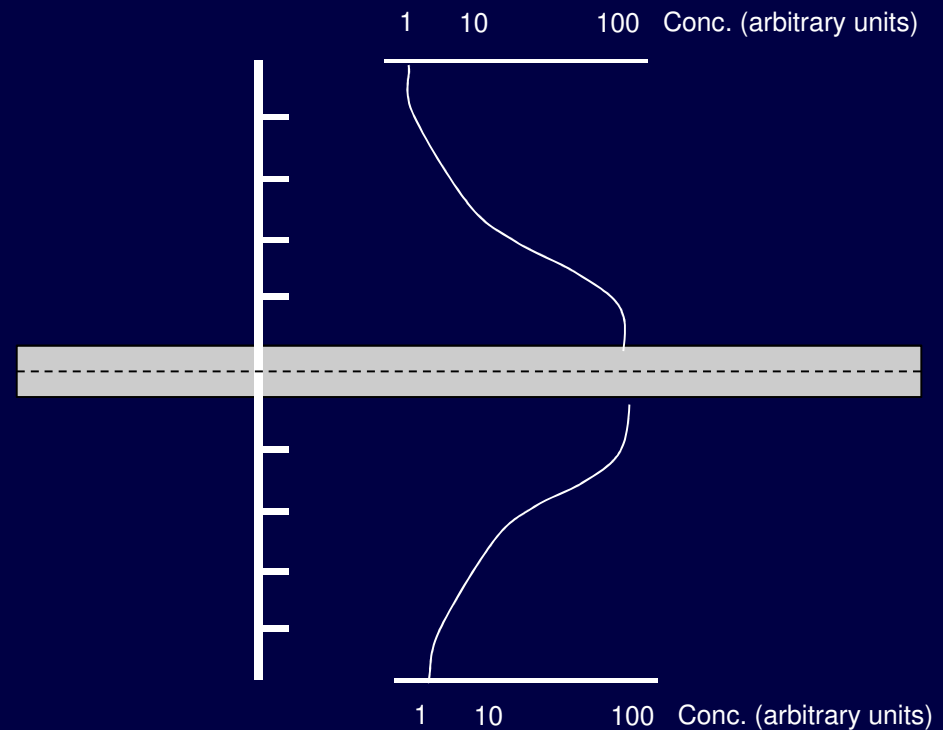
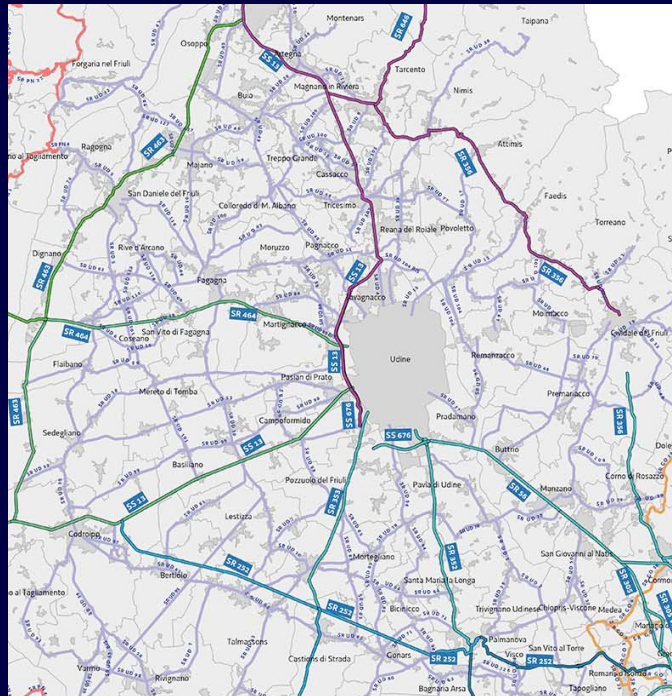
- height of the emitting chimneys;
- wind regime;
- released volume of air;
- concentration of the pollutants at the source.



Higher chimney means a larger area of pollutant dispersion, to which a dilution factor applies (A vs. B). Prevailing winds can determine specific distribution patterns of the pollutants (B vs. C).



LINEAR, such as those connected with extra-urban vehicular traffic; the direct consequences are generally appreciable in a range of a few hundred meters from the road, depending on the intensity of the vehicular traffic.



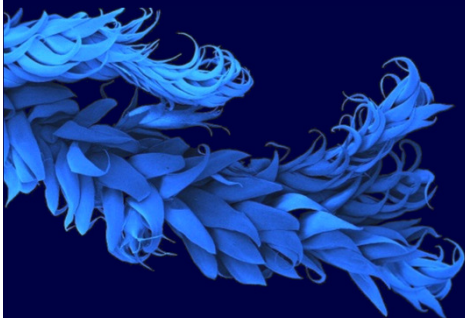
The linear sources correspond to our road network

DIFFUSE, large in size, made up of a large number of small sources distributed over a vast area, such as urban areas (heating, urban traffic), and plants concentrated in industrial areas (in our suburbs often included in the same urban fabric).



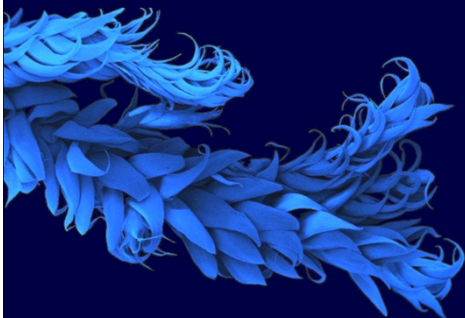


Diffuse sources represent the real challenge of environmental monitoring, because they represent very complex and complex situations. These are problems to be investigated also with biomonitoring techniques due to the intrinsic complexity of the factors involved.



What does our legislator say?

How is pollution defined?



Presidential Decree 24-5-1988 n. 203, Implementation of EEC directives numbers 80/779, 82/884, 84/360 and 85/203 concerning **air quality** standards

Any modification of the normal composition or physical state of atmospheric air, due to the presence therein of one or more substances in quantities and with characteristics such as

- **to alter the normal (environmental and healthy) conditions of the air;**
- to constitute danger or direct or indirect damage to human health;
- to compromise recreational activities and other legitimate uses of the environment;
- to alter biological resources and ecosystems and public and private material goods.

Composizione media dell'aria secca e non inquinata

Costituente	Simbolo/Formula	Frazione molecolare	Per cento <i>in peso</i>	Massa* ($t \cdot 10^9$)
Componenti principali		%		
Azoto	N ₂	78,09	75,37	3.920.000
Ossigeno	O ₂	20,94	23,13	1.200.000
Argon	Ar	0,93	1,41	73.000
Componenti minori		ppm		
Anidride carbonica	CO ₂	330		2.300
Neon	Ne	18		65
Elio	He	5,2		3,8
Metano	CH ₄	1,5		3,7
Cripto	Kr	1		15,2
Idrogeno	H ₂	0,5		0,19
Protossido di azoto	N ₂ O	0,25		1,95
Monossido di carbonio	CO	0,1		0,5
Componenti in tracce		ppb		
Ozono	O ₃	10		0,2
Biossido di azoto	NO ₂	2		0,018
Anidride solforosa	SO ₂	5		0,060

* La massa è quella proprietà per cui i corpi si attraggono fra di loro; la forza con cui la Terra li attira si manifesta come peso

Legislative Decree 3 April 2006, n. 152 (Environmental regulations)

“Any modification of the atmospheric air, due to the introduction into it of one or more substances in quantities and with characteristics such as:

- to harm or constitute a danger to human health or the quality of the environment; or such as
- to damage material assets; or
- to compromise the legitimate uses of the environment.”

LAW 22 May 2015, n. 68

Provisions regarding crimes against the environment.

Official Gazette n. 122 of 05/28/2015

Action is taken at the PENAL CODE level, with consequent inevitable modification of the TUA, Testo Unico sull'Ambiente, Consolidated Law on the Environment

A new Title, **VI bis**, is introduced, defining new crimes and new criminal measures:

- environmental pollution
- environmental disaster
- impediment to environmental controls
- criminal association, including mafia-type, in the environmental field
- omitted reclamation
- trafficking and abandonment of radioactive material

ENVIRONMENTAL POLLUTION

The new article **452-bis** of the penal code punishes with imprisonment from 2 to 6 years and with a fine of 10,000 to 100,000 euro anyone who illegally causes:

- «a significant and measurable impairment or deterioration of the pre-existing state of water or air, or of large or significant portions of the soil and subsoil or of an ecosystem, of biodiversity, including agricultural biodiversity, of flora or fauna.»

There are also several aggravating circumstances for environmental pollution, to reach then the **ENVIRONMENTAL DISASTER**, punished with imprisonment from 5 to 15 years.

ENVIRONMENTAL DISASTER concerns an irreversible alteration of the equilibrium of an ecosystem whose elimination is particularly burdensome and achievable only with exceptional measures.

The offense against public safety is determined with reference both to the relevance of the fact for the extent of the environmental compromise or its harmful effects, and to the number of people offended or exposed to danger.

The environmental disaster is aggravated "if committed in a protected or restricted area or to the detriment of protected animal or plant species."

Some critical points:

- Definitions (e.g. of “impairment” and “deterioration”);
- How extensive? In terms of surface area? Or in depth?
- What measurement systems can be adopted to establish the state of ecosystems?
- How many species do we have to "lose" to speak of "significant impairment or deterioration" to the flora or fauna?

...in the face of some new decisive points:

The authorization requirement is overcome by the observed result!



Our legislators have decided to keep the state of the environment under control by applying two approaches:

- all potentially polluting activities must be authorized.

The authorization procedures provide for maximum air **emission limits**, that should be compatible for maintaining the pre-authorization conditions. This is followed by direct measurements "at the chimney" (...) conducted by specialized (certified) companies or control bodies; communication to local authorities of the measured emission values, for the construction of an emission cadaster at provincial level and a (virtual) reconstruction of the general state of the environment.

To obtain the authorization for the commercialization and/or potential release of new substances, the producer is asked to provide scientific evidence that the new substance is not harmful for the environment. Standard Test Guidelines, approved by international bodies must be applied, which are selected on the basis of the putative quantity of the substance that will be produced during the authorization period and the typology of the substance.

A self-made assessment concerning the (eco-) toxicology of each new substance (or substance family) is thus provided.

The standard environmental control is generally limited to the monitoring, i.e. the quali-quantitative determination of the presence and spatio-temporal distribution in the environment of a (very) small number of pollutants, chosen for their recognized danger, high frequency of emission etc., generally related to the production of energy, i.e. combustion processes, in some points on the territory, having set specific reference limits.

Measurement campaigns limited in time for specific sites or areas can be added, searching for specific classes of pollutants (e.g. potentially toxic elements, polycyclic aromatic hydrocarbons, persistent organic pollutants such as dioxins, dibenzofurans etc.), e.g. around a point emission source.

- il catasto delle emissioni non è immediatamente consultabile, mentre lo è l'*output* della ricostruzione della situazione territoriale, perché ogni Regione deve produrre ogni tre anni un **Piano della Qualità dell'aria**, che si basa largamente sulla stima delle emissioni, che viene poi validata in base alle misurazioni svolte direttamente sul territorio (v. oltre).

Some critical reflections on these points:

- It is necessary to understand how the prescription limits and those defining air quality are set;
- One must ask how significant the controls are in terms of temporal representativeness;
- What are the consequences when the limits are exceeded, and the resulting decision-making processes (who decides what).

In the industrial sector, the direct checks at the source required by law are three per year (Legislative Decree no. 133 of 11 May 2005), and the limits imposed are calculated on an average hourly basis, based on measurements made for at least 30 minutes.

This implies that control sampling is restricted to 0.0375% of the total emission period, 3 half hours over 8000 hours, if we consider a month of plant inactivity.

(The new law provisions provide for detention and a fine for those who cause an impediment to checks.)

In theory, all of us have experience of these checks, because every home heating boiler is subject to:

- Authorization according to the technical characteristics declared by the manufacturer and therefore by the installer;
- Annual inspection by specialized personnel, who certifies that the boiler respects the emission parameters.

RAPPORTO DI CONTROLLO DI EFFICIENZA ENERGETICA TIPO 1 (gruppi termici) Pagina ⁽¹⁾ : di

Climatizzazione invernale Produzione ACS ⁽⁷⁾

Combustibile: GPL Gas naturale
 Gasolio Altro

Modalità di evacuazione fumi: Naturale Forzata

Depressione nel canale da fumo(Pa) ⁽⁸⁾

Dispositivi di comando e regolazione funzionanti correttamente

Dispositivi di sicurezza non manomessi e/o cortocircuitati

Valvola di sicurezza alla sovrappressione a scarico libero

Controllato e pulito lo scambiatore lato fumi

Presenza riflusso dei prodotti della combustione

Risultati controllo, secondo UNI 10389-1, conformi alla legge

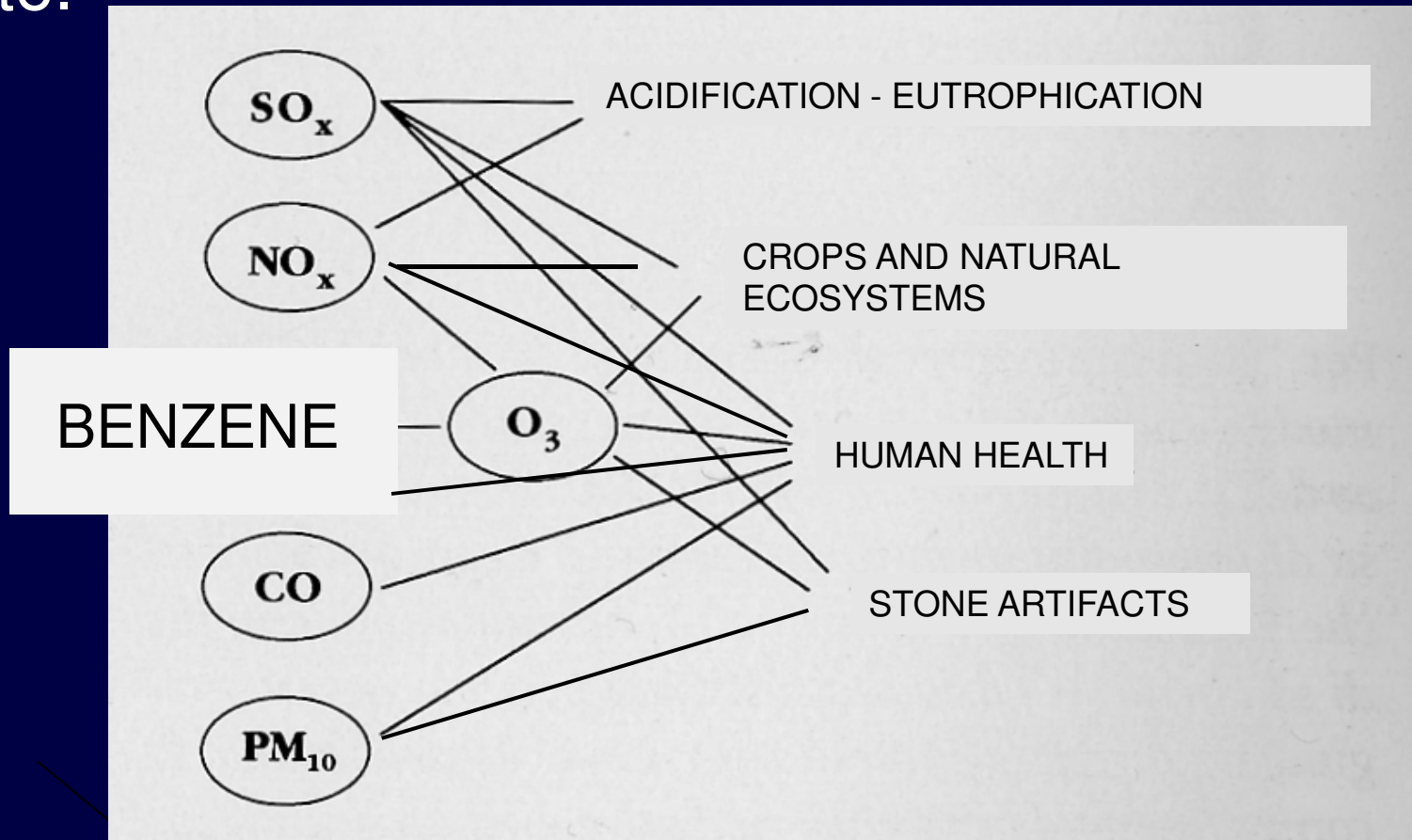
Temperatura Fumi	Temp. Aria comburente	O ₂	CO ₂	Bacharach	CO corretto	Rendimento ⁽⁹⁾ di combustione	Rendimento ⁽⁹⁾ minimo di legge	Modulo termico
..... °C °C % %/...../..... (ppm) % %	

Concerning definition of prescription and air quality limits, these are set on the basis of very long decisional processes, and – sad to say – are more “political” than “scientific”.

Currently the monitoring process on the Italian territory (organised on a regional basis) is based on a network of automatic monitoring gauges.

These structures contain highly sophisticated instrumentation dedicated to the continuous recording of a very small number of pollutants (gaseous and solid), practically ubiquitous ("generalist pollutants"), not specifically linked to individual production processes or anthropic activities, but rather to combustion processes .

There are typically six, five of which are gaseous (CO, SO₂, NO_x, O₃, benzene), one is solid (suspended particulate matter or PM₁₀), although they are not necessarily measured at the same time, at the same site.



These measurement and data recording systems provide extremely precise measurements of pollutant concentrations, as well as equally important meteorological data to describe the complex phenomenon of air pollution:

- wind speed and direction;
- precipitation;
- radiation;
- air temperature.

Data is recorded with varying frequency, but generally at least 1-60 measurements per minute.

The data is then averaged on an hourly, and therefore daily, basis and expressed as mass per unit of volume (e.g. **micrograms per cubic meter**).

Classic statistical descriptors are therefore used, such as daily average value, daily maximum value, percentiles etc.

The chemical-physical measurements are carried out on the basis of standardized analytical methods, using highly standardized instrumental technology, approved by international bodies (e.g. CEN or ISO), that are explicitly cited in official documents.

I. Metodo di riferimento per l'analisi del biossido di zolfo

Ambient Air - Determination of sulphur dioxide — Ultraviolet fluorescence method (Draft International Standard ISO/DIS 10498.2.ISO,1999)

II. Metodo di riferimento per l'analisi del biossido di azoto e degli ossidi di azoto

ISO 7996: 1985 - Ambient Air - Determination of the mass concentration of nitrogen oxides — Chemiluminescence Method.

III.A. Metodo di riferimento per il campionamento del piombo

Fino alla data in cui deve essere raggiunto il valore limite dell'allegato IV, il metodo di riferimento per il campionamento del piombo è quello previsto nell'allegato alla Direttiva 82/884/CEE, come descritto nell'appendice 5, dell'Allegato II al D.P.C.M. 28 marzo 1983. Successivamente a tale data il metodo di riferimento per il campionamento del piombo è quello utilizzato per il PM10 e indicato nella sezione IV.

S.Giovanni al Natisone - SAN GIOVANNI AL NATISONE



data di riferimento: 04/10/2015

legenda

parametro	data	unità di mis.	max media oraria	ora max media oraria	sup. annui max media oraria	max media mobile	ora max media mobile	sup. annui max media mobile	media giorn.	sup. annui max media giorn.	indic. super. giorn.	
Biossido d'azoto	04/10/2015	$\mu\text{g}/\text{m}^3$	11,7	09:00	0	-	-	-	-	-		
Ozono	04/10/2015	$\mu\text{g}/\text{m}^3$	90	14:00	68	78	20:00	68	-	-		
Particelle sospese PM10	04/10/2015	$\mu\text{g}/\text{m}^3$	-	-	-	-	-	-	10	8		

tutta la rete

serie temporale

The law establishes comparing the concentration values in the atmosphere with:

- **Limit values**: the maximum acceptable concentration of a specific pollutant, which can be exceeded a certain number of times;
- **Guiding values**: its maximum desirable concentration. In Italy these values are generally defined at national level, but the Regions can set more stringent values.

Level of attention: it is the concentration of pollutant which, if exceeded persistently over time, can lead to a situation of environmental and health risk;

Alarm level: corresponds to the concentration of pollutant whose exceeding in itself already indicates a situation of environmental and health risk, over which the Mayor of each Municipality has jurisdiction (and criminal responsibility).

There are two areas of interest:

- the protection of human health;
- the protection of ecosystems.

Valore limite	Protezione salute	Media giornaliera	$75 \mu\text{g}/\text{m}^3$ (60% del v.l.)	Max 3 super. anno
Soglia di valutazione superiore	Protezione salute	Media giornaliera	$75 \mu\text{g}/\text{m}^3$ (60% del v.l.)	Max 3 super. anno
	Protezione ecosistemi	Media annuale invernale (1° ott. – 31 mar.)	$12 \mu\text{g}/\text{m}^3$ (60% del v.l.)	
Soglia di valutazione inferiore	Protezione salute	Media giornaliera	$50 \mu\text{g}/\text{m}^3$ (40% del v.l.)	Max 3 super. anno
	Protezione ecosistemi	Media annuale invernale (1° ott. – 31 mar.)	$8 \mu\text{g}/\text{m}^3$ (40% del v.l.)	

(*) in località rappresentative di un agglomerato completo (max 100 km²)

Apparently the limits are lower for the latter, but only because these are expressed on an annual, not daily, basis. In reality – as is obvious to expect – the most stringent limits are those for human health.

The definition of limit values and - where possible - their progressive lowering to improve the state of the environment becomes fundamental.

This is the policy applied by the EU in the last 30 years: penalties are foreseen for those countries that do not improve the air quality of their territories, as demonstrated by recorded data, and specific national policies.

More recently, the data recorded by the automatic gauges have been implemented by modeling: most of our territories are now covered by modeled, theoretical data, not by instrumental data.

The data expected for today and for the following days in the region Friuli Venezia Giulia are calculated with numerical simulation models that take into account the emissions present in the area, the pollution coming from neighboring regions, the forecast meteorological conditions and the actual air quality measurements of the previous days.

- The meteorological simulation is carried out with the WRF model and the SurfPro and GAP modules;
- the emission data are borrowed from the INEMAR regional inventory;
- the simulation of the dispersion, transformations, transport and deposition of pollutants in the atmosphere are carried out with the FARM model.

<https://www.arpa.fvg.it/temi/temi/aria/sezioni-principali/previsioni-qualita-aria-fvg/>

Critical aspects:

- The recording gauges do not always have the instrumentation to record all six pollutants.
- It is assumed that the co-presence of these pollutants has no particular implications (no synergy between them and with other pollutants, certainly present, but not measured, is considered).
- Entire classes of other pollutants (e.g. H₂S, PAHs, dioxins, PTE) are monitored only in exceptional cases, in "hot" areas, for specific problems.
- The control units allow us to know and "keep under control" some of the hot spots in the area, certainly not all.

The undeclared "philosophy" is: "to take measures in the areas most at risk, assuming that the situation a little further away can only be better", due to the dilution and dispersion processes that characterize the air system.

There is a lack of precise legal provisions on the environmental conditions to be met to identify the site for placing a control unit, although a minimum density is established in the area (see below).

The operation of the control units often depends on the willingness to invest considerable sums (the installation and management costs are important).

By the sum of these two facts (high management costs + development of pollutants distribution models), it is not surprising that the number of control units has been drastically decreased.

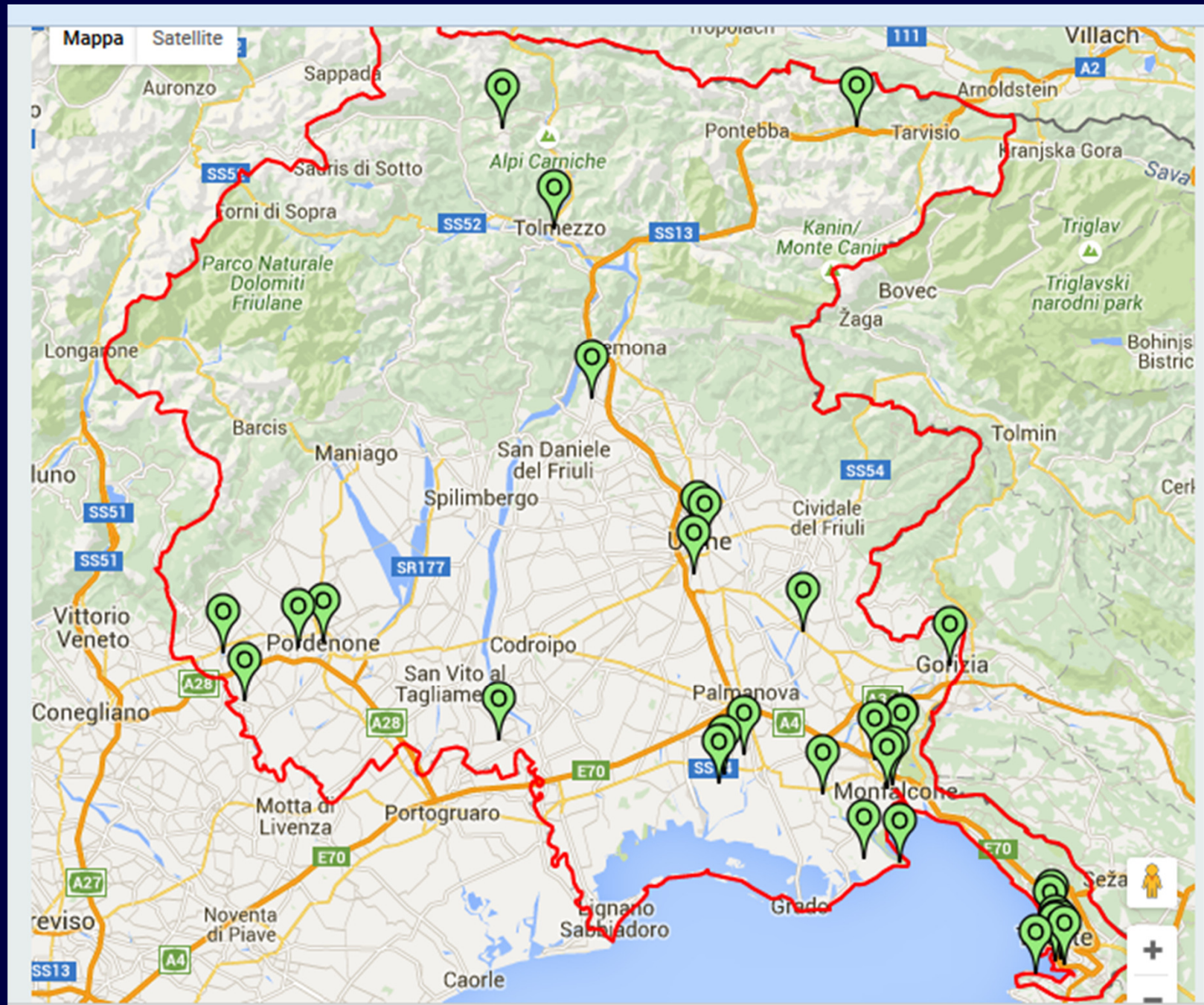
Popolazione dell'agglomerato o zona in migliaia	Se le concentrazioni superano la soglia di valutazione superiore		Se le concentrazioni sono situate tra la soglia di valutazione superiore e inferiore	
	Per inquinanti tranne PM	Per PM (somma di PM10 e PM2,5)	Per inquinanti tranne PM	Per PM (somma di PM10 e PM2,5)
0-249	1	2	1	1
250-499	2	3	1	2
500-749	2	3	1	2
750-999	3	4	1	2
1000-1499	4	6	2	3
1500-1999	5	7	2	3
2000-2749	6	8	3	4
2750-3749	7	10	3	4
3750-4749	8	11	3	6
4750-5999	9	13	4	6
>6000	10	15	4	7

Minimum number of sampling points for the main pollutants (except ozone) according to Directive 2008/50/EC

For the Friuli Venezia Giulia region:

DGR n. 421 4.3.2005 a regional reference network is identified:

9 fixed stations located in the urban centers of the four provincial capitals (3 TS, 2 UD, 1 GO, 1 PN + 1 in Porcia and 1 in Monfalcone) to control the onset of acute pollution episodes, of which 8 provide timely real data relating to ozone concentrations in the air.





Pollutant	P/S	Process	Origin	by-products	Human health	Environment
CO	P	incomplete combustion	org. fuels	-	haemoglobine poison	-
SO ₂	P	combustion, metallurgy	fuels containing S	H ₂ SO ₄	variuos	+++ Acid rains
NO _x	P/S	combustion	fuel cont. N + reaction N ₂ +O ₂	HNO ₃	variuos, oxidative stress	+++ Acid rains
O ₃	S	from NO _x and CO + O ₂	NO+O ₂ at hv+high temp.	-	Oxidative stress	+++
Benzene	P	release	green gasoline	-	cancerogenic	+
PM	P/S	release, phase transformation	wear of materials, combustion	-	Variuos, carrier of dangerous s	+++



SO₂

The main sulfur dioxide emissions derive from:

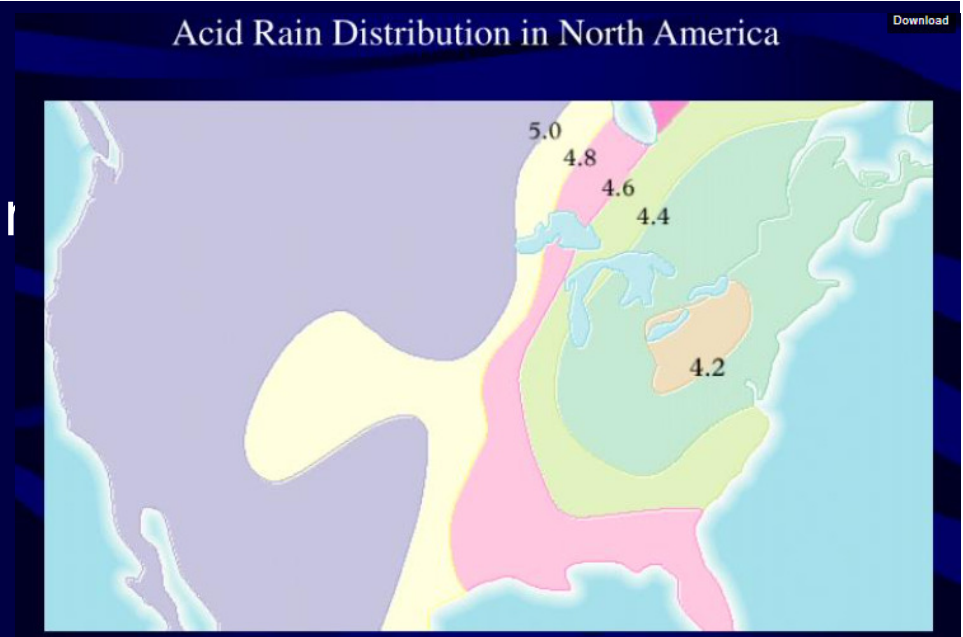
- fixed fossil fuel combustion plants (diesel, fuel oil, kerosene, coal) and wood;
- metallurgical processes (e.g. FeS₂, pyrite);
- production of sulfuric acid (always from the same pyrite...);
- processing of many plastic materials;
- paper industries;
- foundries;
- desulphurisation of natural gases;
- waste incineration.

NO_x

Nitrogen oxides derive from forest fires, the action of lightning and various microbiological processes, but above all from anthropogenic processes during COMBUSTION processes:

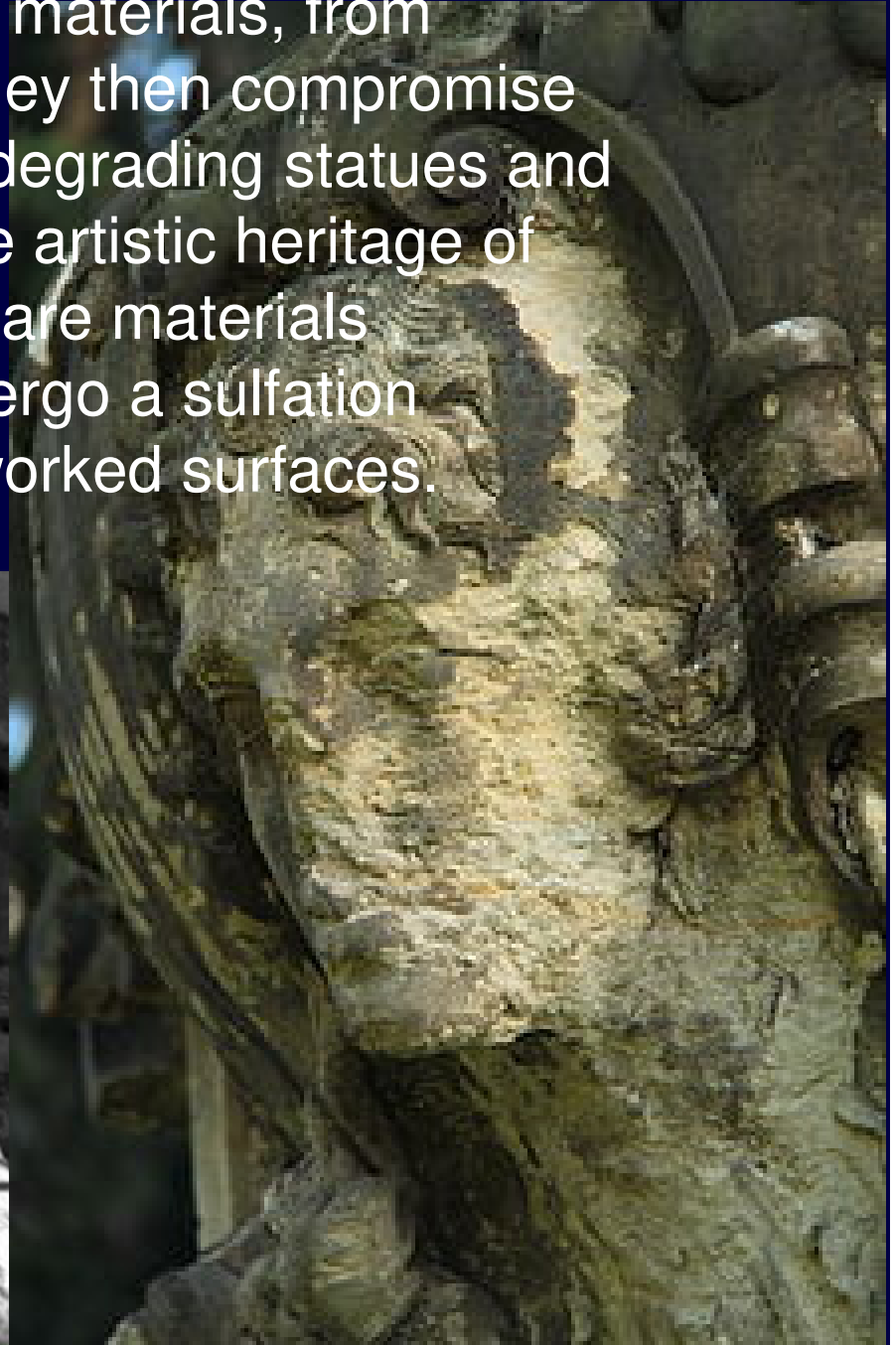
- vehicles that use fossil fuels (both petrol and diesel);
- heating;
- waste incineration;
- blast furnaces.

For decades, rain, snow, fog and dew have been recorded in many areas of the planet with pH values significantly lower than normal (pH 5.6), i.e. between 2.0 and 5.0.



The acid rains (formed directly by the reaction of SO_3 and NO_2 with H_2O in the air) causes the acidification of water bodies (lakes and watercourses), and forest soils; this causes the solubilization of elements (which were previously insoluble and therefore not bio-available), at toxic concentrations (e.g. Al^{3+} , highly toxic), with dramatic damage to the vegetation.

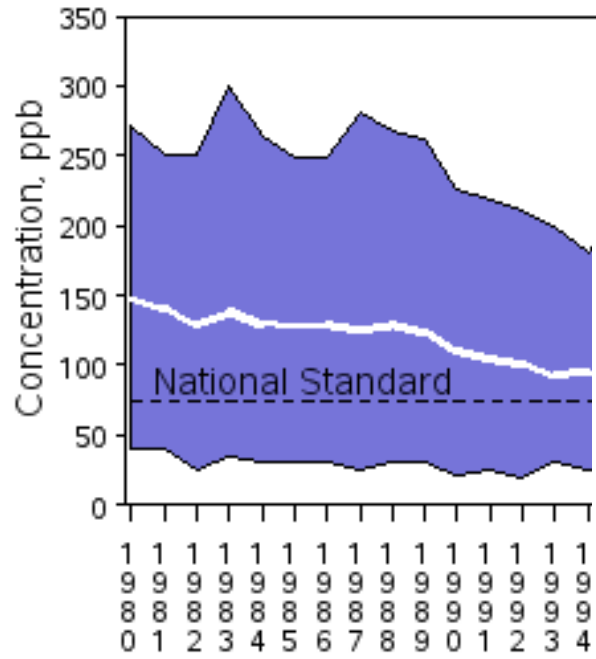
Acid rain accelerates the decay of materials, from construction materials to paints; they then compromise the integrity of the lithic surfaces, degrading statues and sculptures, and more generally the artistic heritage of each nation. Particularly sensitive are materials containing carbonates, which undergo a sulfation process, with serious loss of the worked surfaces.



Data from
EPA, 2014

SO2 Air Quality, 1980 - 2012

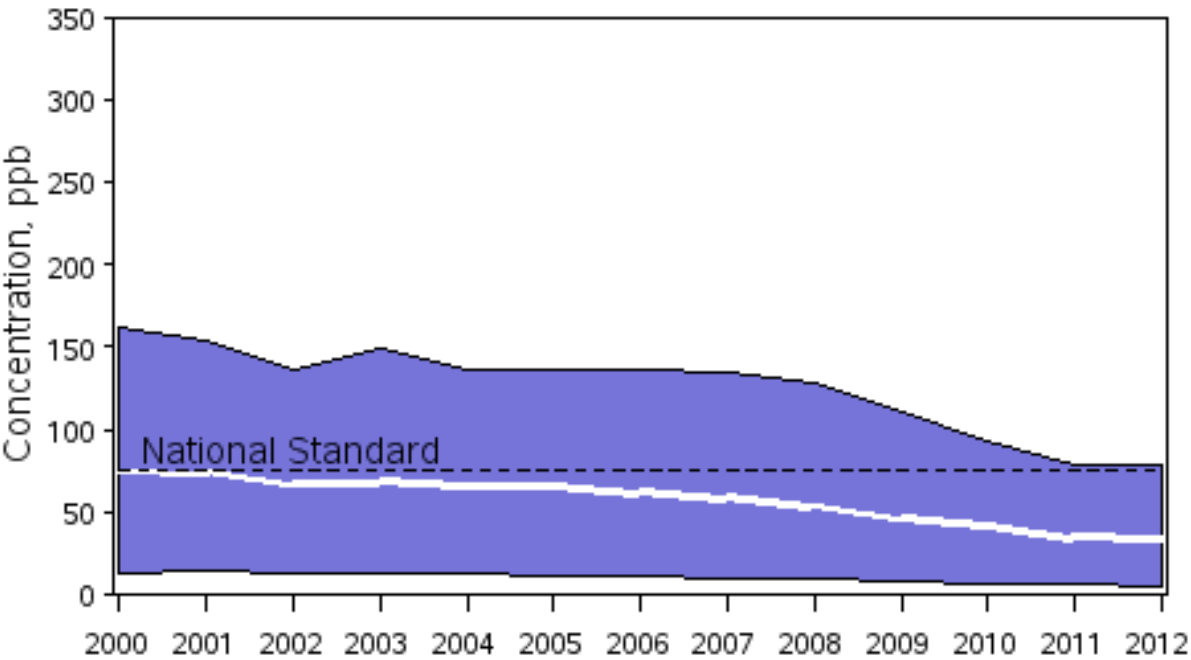
(Annual 99th Percentile of Daily Max 1-Hour Average)
National Trend based on 57 Sites



1980 to 2012 : 78% dec

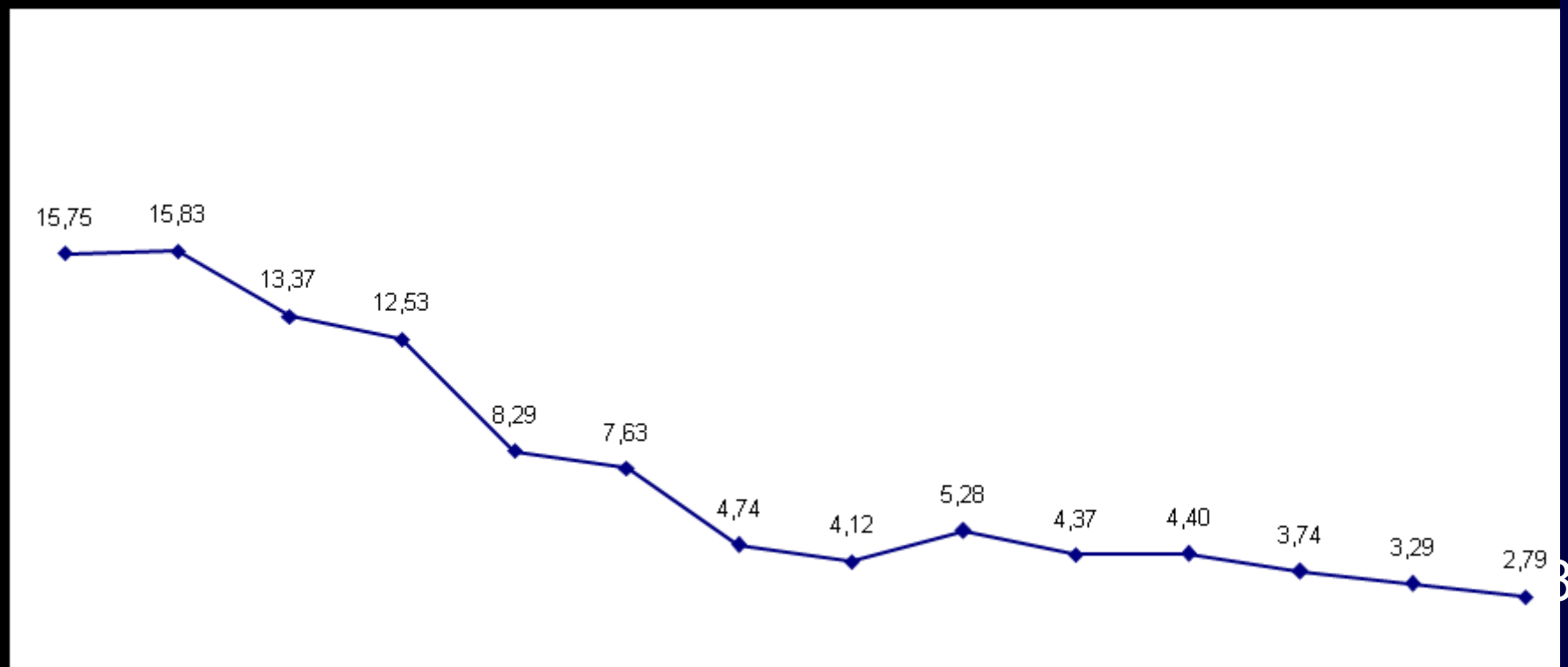
SO2 Air Quality, 2000 - 2012

(Annual 99th Percentile of Daily Max 1-Hour Average)
National Trend based on 260 Sites



2000 to 2012 : 54% decrease in National Average

And Italy?

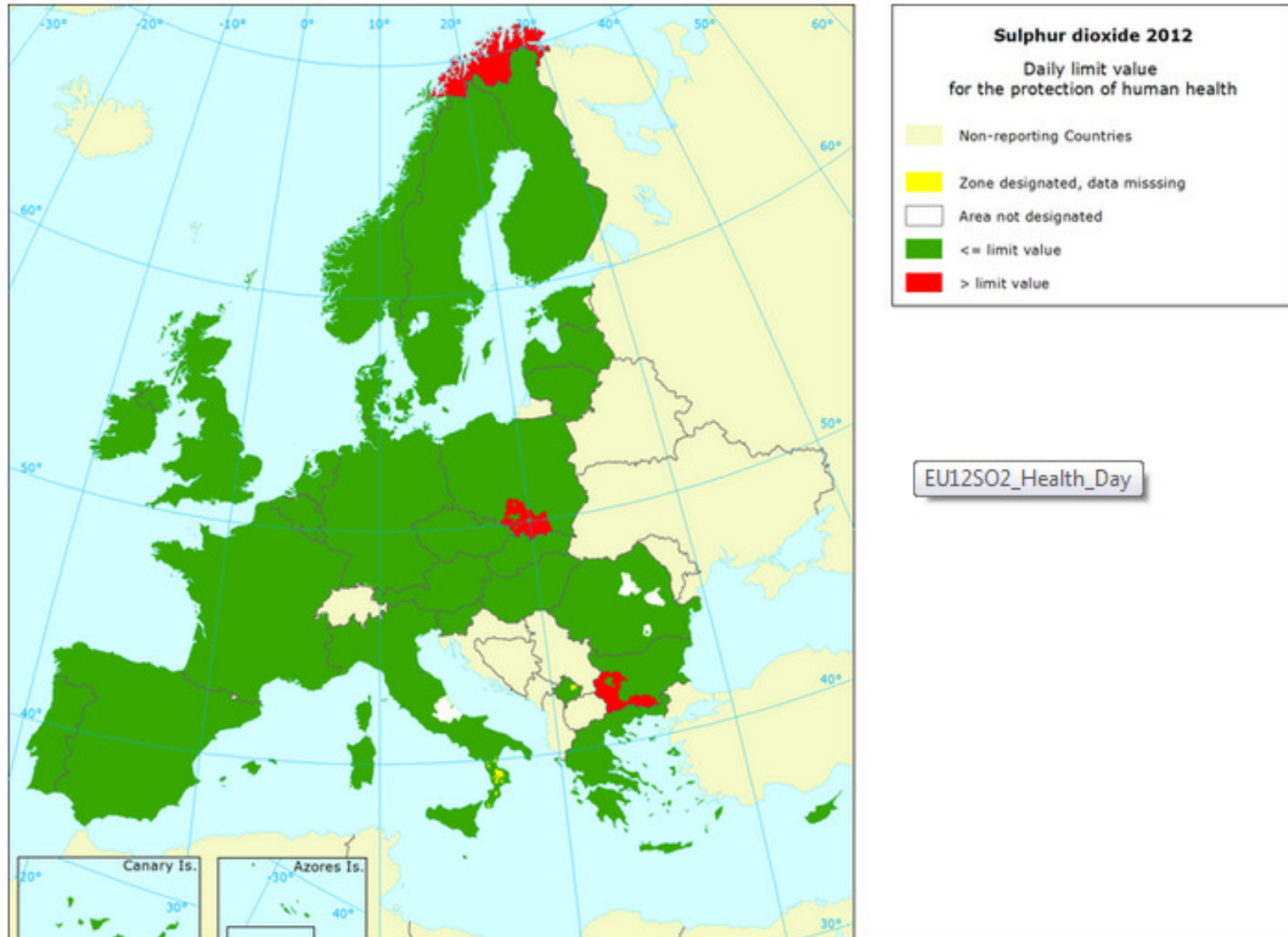


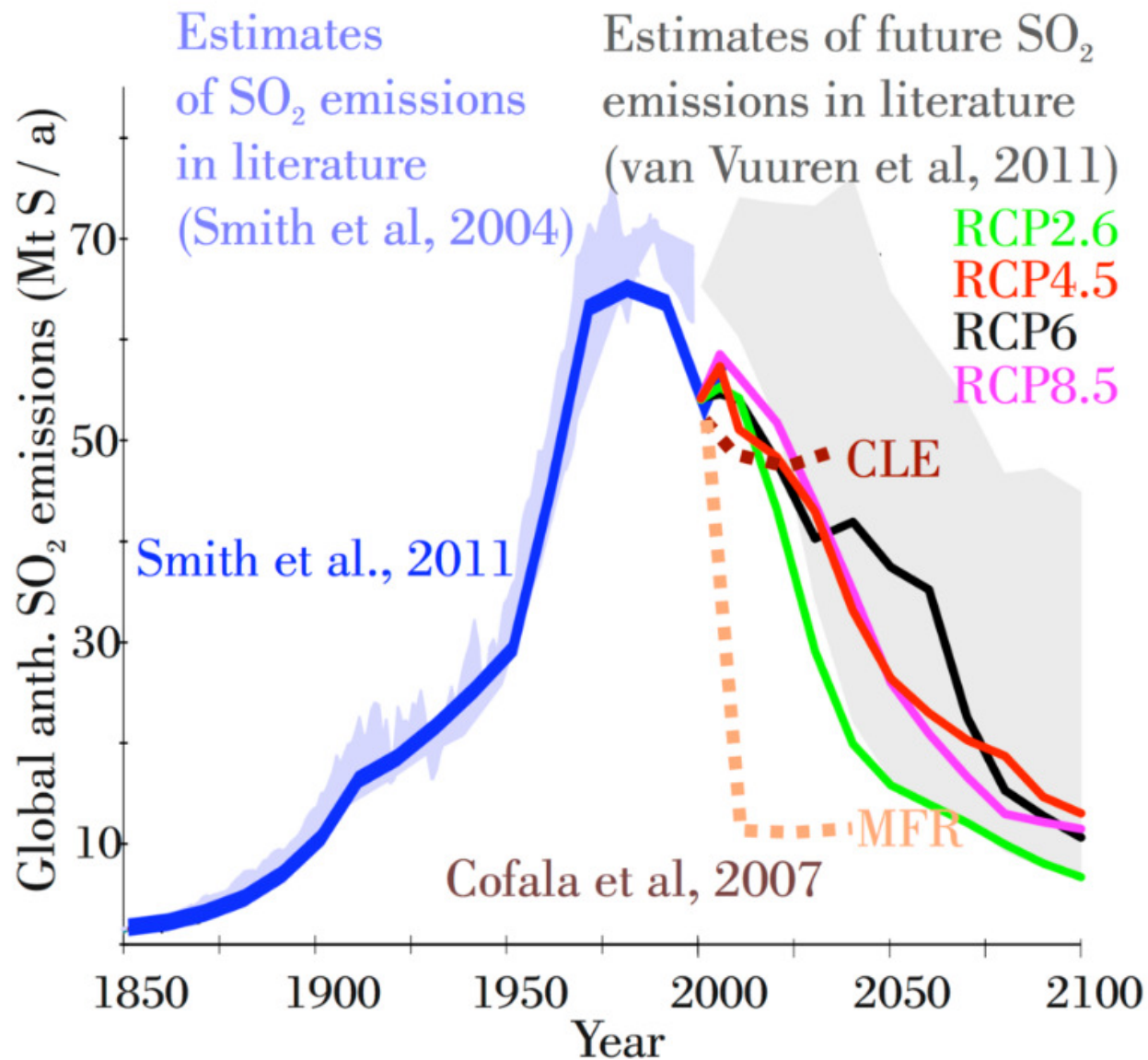
Trend of SO₂ concentration (average daily values, mg m⁻³) in the period 1995-2008 in the city of Udine (NE Italy) [data from: Padovani & Polato, 2010].

This improvement resulted from:

- flue-gas desulfurization, a technology that enables SO₂ to be chemically bound in power plants burning sulfur-containing coal or oil. Most gypsum sold in Europe comes from flue-gas desulfurization;
- increase in the use of methane, in industrial processes and in building heating systems;
- Taxation of sulphur-rich coal, oil or other fossil fuels.

In the air quality directive (2008/EC/50) the EU has set two limit values for sulphur dioxide (SO₂) for the protection of human health: the SO₂ hourly mean value may not exceed 350 micrograms per cubic metre ($\mu\text{g}/\text{m}^3$) more than 24 times in a year and the SO₂ daily mean value may not exceed 125 micrograms per cubic metre ($\mu\text{g}/\text{m}^3$) more than 3 times in a year.



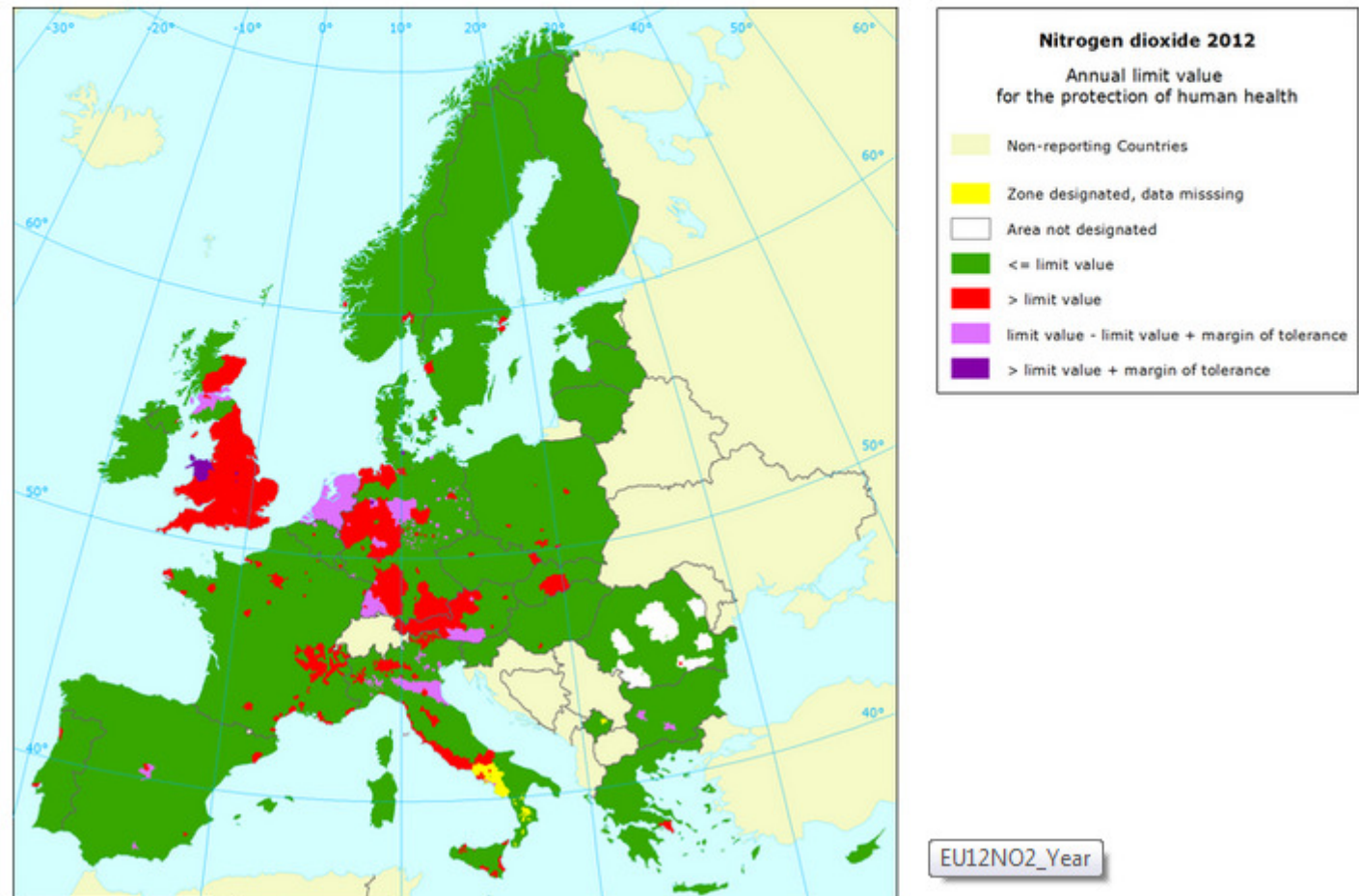


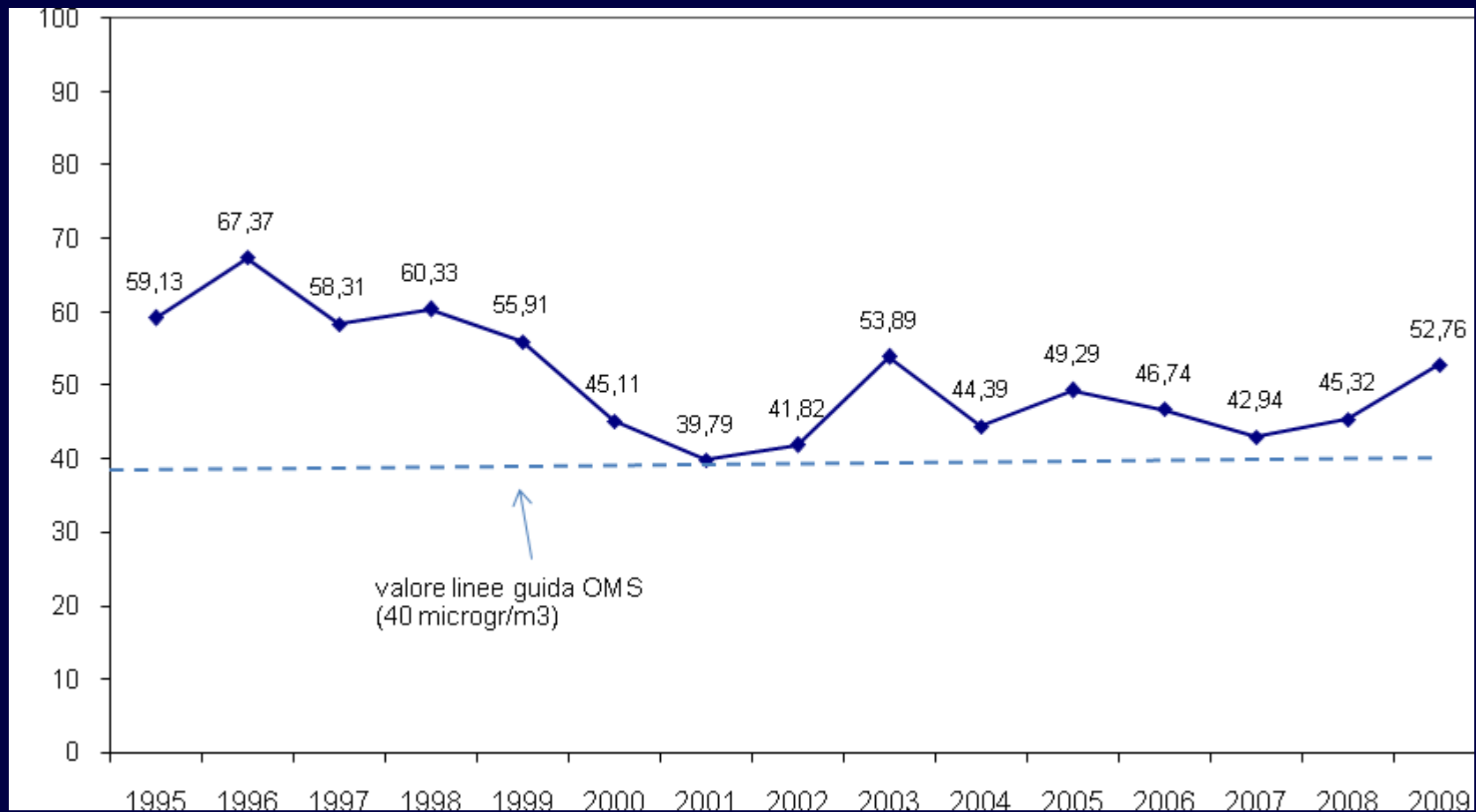
As of 2006, China was the world's largest sulfur dioxide polluter, with 2015 emissions estimated to be 25,490,000 short tons (23.1 Mt). This amount represents a 27% increase since 2000, and is roughly comparable with U.S. emissions in 1980.

A collection of estimates of past and future anthropogenic global sulphur dioxide emissions.

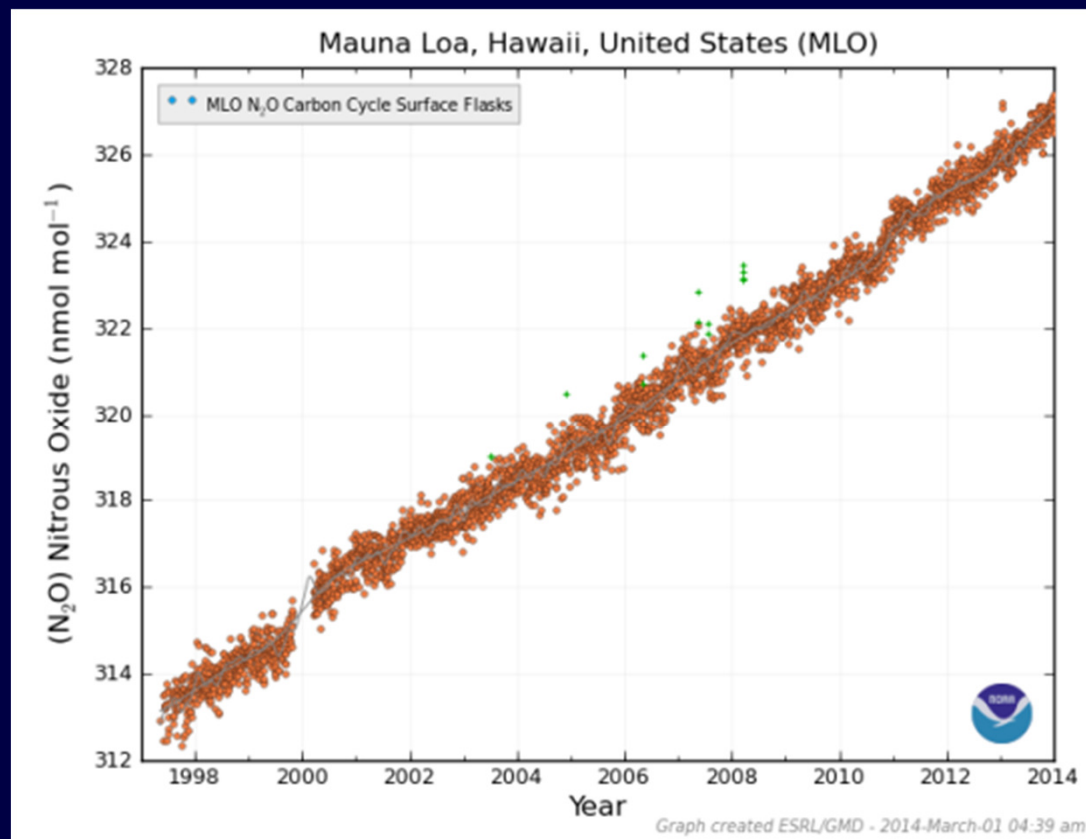
For NO_x , the situation is less positive.

In the air quality directive (2008/EC/50) the EU has set two limit values for nitrogen dioxide (NO_2) for the protection of human health: the NO_2 hourly mean value may not exceed 200 micrograms per cubic metre ($\mu\text{g}/\text{m}^3$) more than 18 times in a year and the NO_2 annual mean value may not exceed 40 micrograms per cubic metre ($\mu\text{g}/\text{m}^3$). These limit values come into force for concentrations measured from 1.1.2010 so during 2009 a margin of tolerance equal to an annual mean value of 42 micrograms per cubic metre ($\mu\text{g}/\text{m}^3$) is still in place.

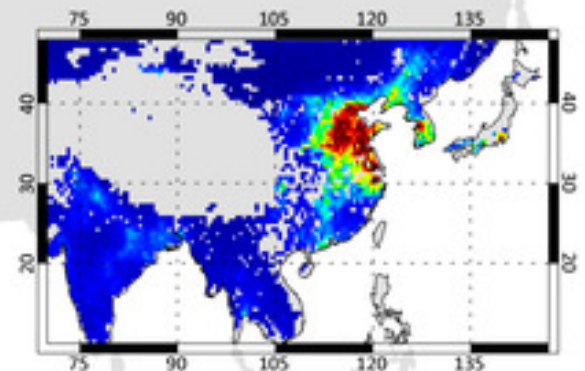
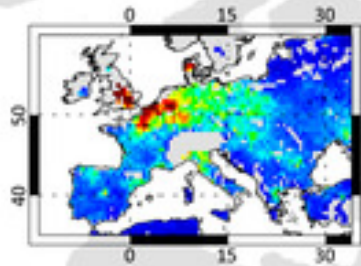
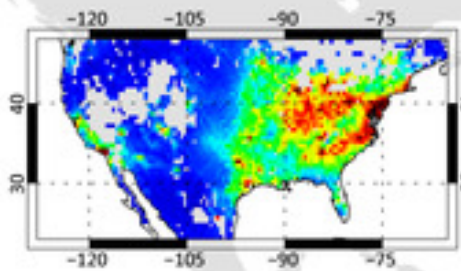




Trend of NO₂ concentration (average daily values, mg m⁻³) in the period 1995-2008 in the city of Udine (NE Italy) [data from: Padovani & Polato, 2010].



Satellite derived trends of anthropogenic NO_x and CO₂ emissions



North America
Europe

NO_x -2.7%/a
CO₂ -1.3%/a



NO_x +5.8%/a
CO₂ +9.8%/a

East Asia

