

Methods of Measuring Sulfur Dioxide, Dustfall and Suspended Matter in City Air, and their Use in the Study of Air Pollution in Italy *

F. L. PETRILLI¹

This paper presents a comparative survey of the methods and apparatus used in Italy, particularly in Genoa, for measuring the three main components of city air pollution—sulfur dioxide, dustfall and suspended matter.

The most frequently employed devices for sampling sulfur dioxide are the lead-peroxide and volumetric apparatuses, as developed by the British Department of Scientific and Industrial Research. For the collection of dustfall, the British standard deposit gauge is widely used; in Genoa, a simple, low-cost type of dustfall collector has been tried in combination with that gauge, and good results have been obtained. The measurement of suspended matter is effected by the thermal precipitator, electrostatic precipitator and konimeters of different types, in addition to the classic method of filtration through various media. In Genoa, suspended matter is monitored by automatic filter-paper samplers and directional samplers. The use of membrane filters for counting dust particles has proved particularly satisfactory.

All these techniques are described in detail, and their results are subjected to statistical analysis.

The problem of air pollution has received attention in Italy since 1954. In that year the first results of organized research into the air pollution caused by industrial plants in the Mestre area were made known by the Institute of Hygiene of the University of Padua. At almost the same time the problem was taken up by the Institutes of Hygiene of the Universities of Genoa and Milan, and later by those of the Universities of Bologna, Perugia and Rome.

Whether air pollution is caused by industrial plants, heating systems or city traffic, in each case sulfur dioxide, dustfall and suspended matter are involved. Thus, although we do not wish to minimize the interest of other special research on certain sources of air pollution, such as the important investigations of carbon monoxide from motor traffic (it is enough to recall that a concentration of 400 p.p.m. of carbon monoxide was recorded in a street tunnel in Genoa in which peak-hour motor

traffic is very heavy), research workers in Italy have focused their attention on the three above-mentioned factors.

At first we confined ourselves to the use of methods in which experience had been acquired abroad, particularly in Great Britain. Having adopted the apparatus suggested by the Department of Scientific and Industrial Research (DSIR) (deposit-gauges, lead-peroxide apparatus, volumetric devices, etc.), we were able, from the outset, to standardize our research sufficiently for comparison with work done elsewhere in this field. Subsequently, we employed other techniques and methods of analysis, using, in particular, sampling systems suitable for obtaining information on short-life variations in concentrations of individual pollutants. Details of the various methods adopted and some of the results obtained are given below, though it has not been possible in the space available to go fully into all the data collected.

SULFUR DIOXIDE

Measurements of sulfur dioxide carried out by means of lead-peroxide apparatus have yielded a

* Paper submitted to a Symposium on Epidemiological Aspects of Air Pollution, convened by the WHO Regional Office for Europe in December 1960.

¹ Director, Institute of Hygiene, University of Genoa, Italy.

remarkable quantity of data. On the whole, the results from 18 survey stations in Genoa (Table 1 and Fig. 1) are sufficiently indicative; they refer to the period from November 1954 to November 1960. For each zone the average summer levels (April-September, when heating plants are not working) and the average winter levels (October-March) are reported. Two inferences can immediately be drawn:

(1) There is a marked degree of steady pollution in those districts situated in the neighbourhood of typically industrial zones.

(2) Pollution is relatively modest, though greater during the winter months, in residential districts.

The lead-peroxide measuring apparatus is known to be open to criticism on the grounds that it is affected by temperature, relative humidity and air movement, so that the results it gives are not absolute but only relative. In my opinion, however, this does not detract much from its value.

TABLE 1
SULFUR DIOXIDE EMISSION IN GENOA (1954-1960):
MEASUREMENTS AT 18 SITES BY DSIR LEAD-PEROXIDE
APPARATUS

Site of instrument	Summer (mg/100 cm ² /day)	Winter (mg/100 cm ² /day)
1	0.255	1.236
2	0.305	1.402
3	0.179	0.776
4	1.062	2.222
5	0.945	1.917
6	0.819	2.143
7	0.885	1.840
8	1.047	2.191
9	1.139	2.391
10	0.089	0.389
11	0.619	1.342
12	0.392	1.488
13	0.111	0.350
14	1.148	3.585
15	0.465	1.134
16	0.614	1.557
17	0.403	1.390
18	0.074	0.247

We have used this device simultaneously with other apparatus on several occasions and have found that, practically speaking, the final results always tally. Thus, when the PbO₂ apparatus was indicating high levels of SO₂, other more expensive and sensitive forms of apparatus were also indicating high values, and *vice versa*. We have also found that by limiting exposure to 15 days, we can more rapidly obtain information of some practical interest in that it can give an idea of the degree of pollution existing in a given area, which is useful in establishing the most suitable sites for other apparatus (see Table 2). Moreover, we have found that the correction factor suggested by British authors for the conversion of the conventional terms of milligrams per 100 square centimetres per day into parts per million (p.p.m.) can be of some use.

Finally, we have come to the conclusion that the lead-peroxide method, although open to criticism from some standpoints, should not—owing to its simplicity and very low cost of upkeep and analysis—be abandoned until a more advantageous device can be found. The data supplied by it may always prove valuable as a reference in any type of investigation, even for a well-equipped laboratory.

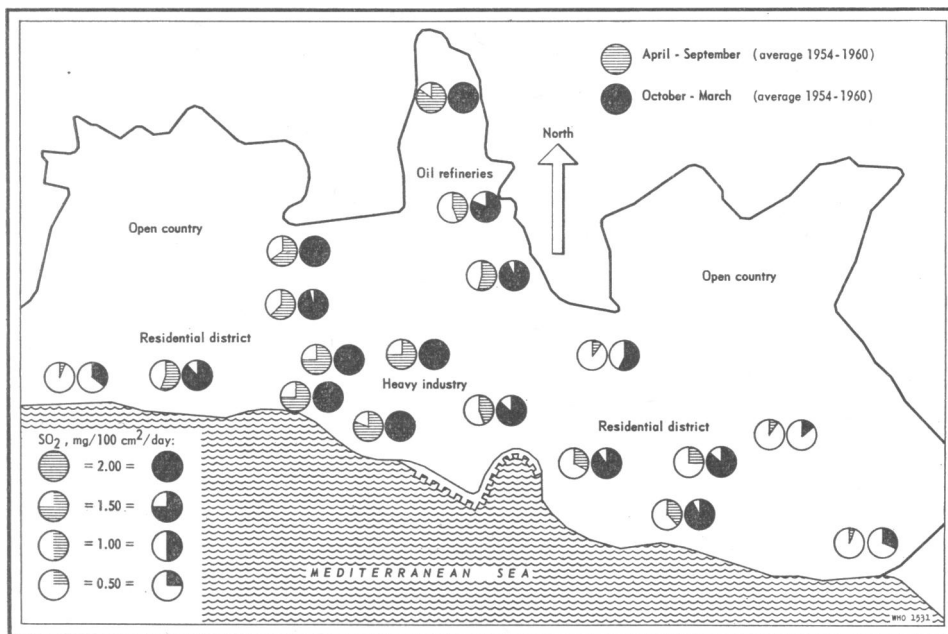
TABLE 2
SULFUR DIOXIDE EMISSION IN GENOA (1958-1959):
MEASUREMENTS BY TWO LEAD-PEROXIDE
APPARATUSES ^a

Month	Monthly measurement (mg/100 cm ² / day)	1st 15 days of month (mg/ 100 cm ² /day)	2nd 15 days of month (mg/ 100 cm ² /day)
January	1.05	1.08	1.03
February	1.15	1.30	1.10
March	0.91	0.90	0.85
April	0.82	0.87	0.78
May	1.08	1.18	1.04
June	0.91	0.96	0.88
July	0.85	0.89	0.72
August	0.48	0.50	0.44
September	1.19	1.27	1.05
October	1.00	0.98	0.93
November	1.13	1.10	1.06
December	1.21	1.32	0.99

^a The two apparatuses were only 15 feet apart.

FIG. 1

SULFUR DIOXIDE EMISSION IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY DSIR LEAD-PEROXIDE APPARATUS (mg/100 cm²/day)



Others methods frequently employed in Italy are briefly discussed below.

Sampling system based on an air pump, gas meter and gas-washing bottles

This system is employed either for short-term sampling (30-60 minutes) or for long-period sampling (up to 24 hours). The reagents most often used are diluted hydrogen peroxide solution (3 %), an alkaline iodine solution (0.001 N), and a sodium tetrachloromercurate (0.1 M) solution. Cauer's, Pregl's, Drechsel's and Jena's gas-washing bottles are the types which are most frequently employed. The volume of the reagent varies, according to the capacity of the sampling bottle, from 10 ml to over 100 ml. The most common analytical methods are titration with alkaline solution, the turbidimetric method, the gravimetric method and the colorimetric method.

The air sampling rate varies between 0.5 l/minute for small absorption bottles and 10 or more l/minute for Cauer's bottles. In Genoa we at present employ sampling apparatus consisting of an air pump, gas meter and Jena's gas-washing bottles. The reagent in which the sulfur dioxide is scrubbed is a 0.1

sodium tetrachloromercurate solution. The determination is based on the reading of the maximum absorption at 560 m μ of the red-violet colour produced when a *p*-rosaniline hydrochloride-hydrochloric acid mixture (0.04 % dye + 6 % concentrated acid) and formaldehyde (0.2 %) are added to the sampling solution. Table 3 and Fig. 2 show the results of samplings carried out in the various districts of Genoa already indicated (Fig. 1) in connexion with the surveys using the PbO₂ apparatus; such samplings were taken in accordance with the previously mentioned methods. The figures shown are the average of those obtained by numerous samplings both for the months when there is no domestic heating (April-September) and for the colder months (October-March).

Apparatus for continuous analysis and automatic recording of concentrations

In Italy we use the well-known Thomas autometer, of which, as far as we know, there is one in Genoa and one in Bologna. The autometer records: (a) the concentration of the pollutant at any given instant; (b) an average integrated reading every

FIG. 2

SULFUR DIOXIDE EMISSION IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY DSIR VOLUMETRIC APPARATUS (p.p.m.)

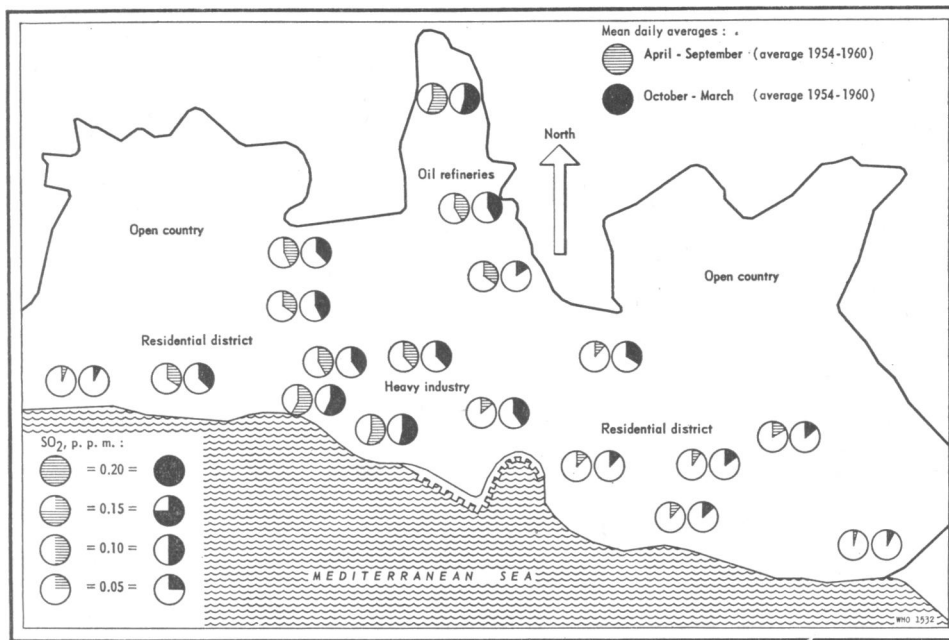


FIG. 3

SULFUR DIOXIDE EMISSION IN GENOA : MEASUREMENTS AT 18 SITES BY THOMAS AUTOMETER (p.p.m.)

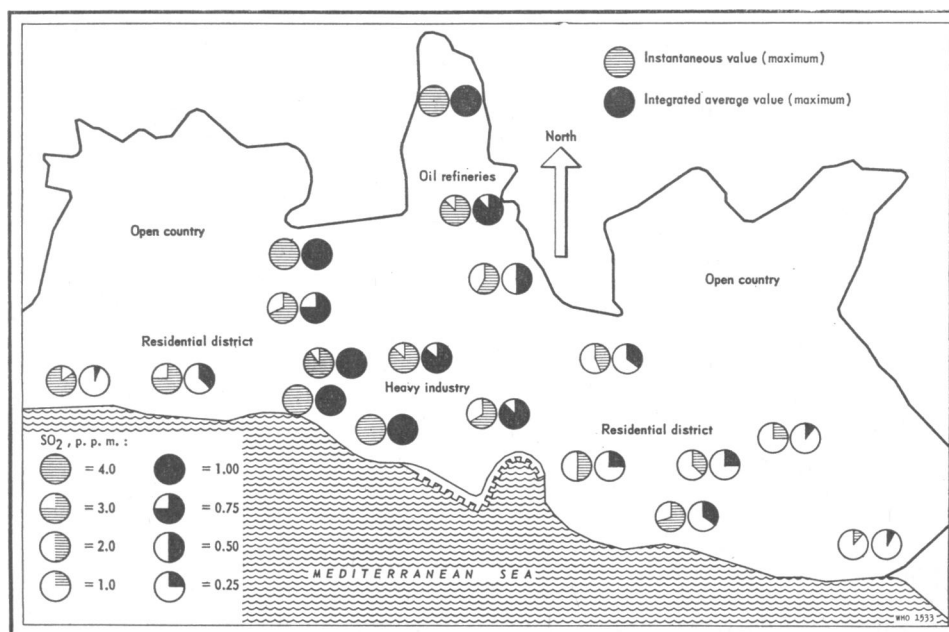


TABLE 3
SULFUR DIOXIDE EMISSION IN GENOA (1954-1960) :
MEASUREMENTS AT 18 SITES BY DSIR VOLUMETRIC
APPARATUS

Site of instrument	Summer (p.p.m.)	Winter (p.p.m.)
1	0.02	0.03
2	0.01	0.04
3	0.02	0.04
4	0.08	0.07
5	0.08	0.08
6	0.09	0.07
7	0.06	0.08
8	0.12	0.10
9	0.11	0.14
10	0.01	0.02
11	0.07	0.09
12	0.03	0.03
13	0.04	0.04
14	0.12	0.10
15	0.09	0.08
16	0.07	0.04
17	0.03	0.08
18	0.01	0.02

half-hour. Fig. 3 shows the instantaneous and average peaks recorded by the autometer in the same districts as were surveyed with the other apparatus. This apparatus seems to be particularly practicable for recording concentrations between

0 and 5 p.p.m., and its sensitivity is better than 0.05 p.p.m.. The use of this apparatus has been made easier by introducing some simple modifications. The height of the autometer is reduced by setting the recorder at the back and by decreasing the size of the reagent container. A truck is used to carry the apparatus.

In Genoa we also use a semi-automatic apparatus for direct quick reading of the sulfur dioxide concentration. This apparatus has been designed by the British Central Electricity Generating Board (CEGB) and allows four samplings per hour.

In Italy we also use some sequential absorption apparatus which, in principle, follows the models by Cholak and Haagen-Smit. As yet, we have not had sufficient experience of this method and all that can be said is that the first data seem to be satisfactory.

The various apparatuses for measuring sulfur dioxide are also used simultaneously if the data thus obtained are required for study or checking purposes. In some of our Genoa research, for instance, we have employed at the same time several PbO_2 apparatuses, aspiration methods based on volumetric apparatus of the DSIR type, as well as the CEGB apparatus and the Thomas autometer. Table 4 gives some sample readings from one of the tests relating to measurements of the diffusion of sulfur dioxide from an isolated source.

Perusal of these data will reveal not only the diversity, *ceteris paribus*, of the figures obtained by the various techniques employed, but also the extent to which the duration of sampling affects the results as a whole. Thus, while the autometer's instantaneous readings have indicated concentrations greater than 5 p.p.m., under the same conditions the

TABLE 4
SAMPLING OF SULFUR DIOXIDE EMISSION FROM AN ISOLATED SOURCE USING FOUR
DIFFERENT METHODS

Apparatus	Sampling time	Sample volume	Concentration	
			Minimum	Maximum
Lead-peroxide	1 month	—	0.11 mg/100 cm ² /day ^a	2.95 mg/100 cm ² /day ^a
Volumetric	24 hours	600 l/hour	0.05 p.p.m.	0.85 p.p.m.
CEGB	10 minutes	600 l/hour	0.01 p.p.m.	2.50 p.p.m.
Thomas autometer	Instantaneous	566 l/hour	0.05 p.p.m.	>5.00 p.p.m.

^a The concentrations recorded by the PbO_2 apparatus, as corrected according to the British national average factor, may also be indicated : 0.002 p.p.m. and 0.098 p.p.m.

volumetric apparatus has indicated maximum concentrations lower than 1 p.p.m.

Further, it must be remembered that what is important for the practical purposes of an epidemiological inquiry is not only the average value derived from a long period of sampling, but also the temporary pollution conditions which may be suspected as the cause of a sudden outbreak of some affection whose consequences might range from simple variation of respiratory and cardiac frequency to an attack of asthma. Many a time we have noticed high concentrations of SO_2 , lasting, however, only over a short period. The effect of such short-term concentrations is one of the objects of research at the Genoa University Institute of Hygiene. For this kind of work continuous recording and sampling apparatus is ideal.

Our experience of surveying sulfur dioxide pollution has led us to conclude that:

(1) The lead-peroxide apparatus is unquestionably practical and useful, and it is still advisable to employ it in spite of the reservations that may be made from a strictly scientific standpoint. The very practicality of this apparatus makes its method of application worth standardizing—e.g., height from the ground, distance from nearby obstacles of whatever nature, number of apparatuses in proportion to the area to be examined, choice of the reagent (lead peroxide), which should be the same for all laboratories so as to achieve greater uniformity in results.

(2) The continuous survey of sulfur dioxide concentrations by means of an automatic or semi-automatic recorder for periods of up to 24 hours must, however, also be carried out at the same time as the lead-peroxide method. In fact, an epidemiological inquiry cannot be considered satisfactory unless the behaviour of the suspected noxious factor and that of one or more individuals exposed to it are examined on a corresponding scale.

(3) Standardization of the latter method is more difficult and complicated than in the case of the lead-peroxide apparatus. It would therefore be advisable, as soon as possible, to study the best forms of research by means of appropriate apparatus and identical methods of sampling, with the aim of obtaining data for an eventual standardization project.

DUSTFALL

Dustfall measurements are usually made with the British standard deposit gauge (DSIR). Tables 5-10

and Fig. 4-6 give the results obtained employing these gauges in the 18 areas of the city already referred to in connexion with the measurement of sulfur dioxide. These figures represent the average for the two periods, April-September and March-October 1954-1960. The graphs show only the total matter collected (insoluble + soluble substances), combustible matter and iron (expressed as Fe_2). Determination of the iron content was always made from samples beyond all the usual DSIR determinations. From the data recorded a clear difference between the dustfall for typically residential and that for typically industrial areas can also be observed.

In the latter areas the rates of dustfall recorded were sometimes more than 10 times greater than those in the former areas. Up to now it has not been possible to discern a significant difference in the residential areas between the dustfall collected annually from April to September (summer months) and that collected from October to March (winter months). However, in the vicinity of industrial plants, a marked increase of dustfall could be noted during the summer period. These phenomena can easily be explained by the topographic and meteorological conditions. The larger quantities of dustfall collected in some areas near iron and steel plants must be considered in the light of the fact that the prevailing winds blow towards these areas in April-September, and away from them during the winter.

The figures relating to the iron content of the insoluble matter collected are interesting. Fig. 6 clearly indicates the area of the city or its immediate neighbourhood in which there is a larger amount of industry with correspondingly high figures for the amount of iron.

In Genoa, following many tests with other types, a different deposit gauge (Genoa type), close to the British standard models, has now been employed for a long time. This new gauge is intended as a more practical and economical measuring device, constructed as a single cylindrical, glass collector (292 mm high), the upper diameter corresponding to that of the collecting aperture, which is a little narrower than the rest of the collector (95 mm). This gauge, which costs about one-twentieth of the British standard gauge, can be easily moved and located in a number of different areas within a short space of time. When being carried around, the gauge is hermetically sealed by means of a plastic cover. The internal corners are rounded and the matter collected can be easily and rapidly extracted. Finally, the collecting aperture, which is somewhat

TABLE 5

TOTAL MATTER DEPOSITED (INSOLUBLE AND SOLUBLE) IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY BRITISH STANDARD DEPOSIT GAUGE

Site of instrument	Summer (g/100 m ² /month)	Winter (g/100 m ² /month)
1	661	670
2	377	383
3	548	476
4	1467	1377
5	1965	1158
6	1138	755
7	1185	760
8	6273	3119
9	7520	4392
10	489	339
11	754	731
12	583	542
13	577	342
14	753	885
15	513	455
16	687	578
17	647	423
18	448	312

TABLE 7

COMBUSTIBLE MATTER DEPOSITED IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY BRITISH STANDARD DEPOSIT GAUGE

Site of instrument	Summer (g/100 m ² /month)	Winter (g/100 m ² /month)
1	103	86
2	69	59
3	128	92
4	286	134
5	470	518
6	162	119
7	395	147
8	1275	513
9	1686	865
10	71	52
11	193	106
12	51	51
13	97	87
14	104	222
15	69	65
16	131	184
17	142	214
18	53	62

TABLE 6

INSOLUBLE MATTER DEPOSITED IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY BRITISH STANDARD DEPOSIT GAUGE

Site of instrument	Summer (g/100 m ² /month)	Winter (g/100 m ² /month)
1	305	304
2	167	137
3	374	270
4	918	806
5	1548	1263
6	742	455
7	829	481
8	5590	2618
9	6897	3815
10	258	151
11	804	446
12	177	152
13	264	214
14	441	510
15	294	226
16	458	402
17	376	389
18	205	145

TABLE 8

ASH DEPOSITED IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY BRITISH STANDARD DEPOSIT GAUGE

Site of instrument	Summer (g/100 m ² /month)	Winter (g/100 m ² /month)
1	202	218
2	98	78
3	246	178
4	632	672
5	1078	745
6	580	336
7	434	334
8	4315	2105
9	5211	2950
10	187	99
11	612	340
12	126	101
13	167	127
14	337	288
15	225	161
16	327	218
17	234	175
18	152	83

TABLE 9

IRON (Fe) DEPOSITED IN GENOA (1954-1960) :
MEASUREMENTS AT 18 SITES BY BRITISH STANDARD
DEPOSIT GAUGE

Site of instrument	Summer (g/100 m ² /month)	Winter (g/100 m ² /month)
1	35	25
2	18	12
3	39	23
4	176	258
5	361	270
6	189	125
7	210	132
8	1418	756
9	1832	1382
10	42	20
11	162	78
12	26	22
13	26	30
14	84	62
15	43	26
16	72	43
17	46	40
18	39	18

TABLE 10

TOTAL DISSOLVED MATTER DEPOSITED IN GENOA
(1954-1960) : MEASUREMENTS AT 18 SITES BY
BRITISH STANDARD DEPOSIT GAUGE

Site of instrument	Summer (g/100 m ² /month)	Winter (g/100 m ² /month)
1	356	329
2	210	284
3	184	205
4	544	595
5	374	339
6	369	317
7	361	295
8	699	554
9	646	634
10	233	201
11	348	284
12	431	450
13	310	154
14	316	375
15	212	224
16	243	261
17	255	203
18	215	198

FIG. 4

TOTAL MATTER (INSOLUBLE AND SOLUBLE) DEPOSITED IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY
BRITISH STANDARD DEPOSIT GAUGE (g/100 m²/month)

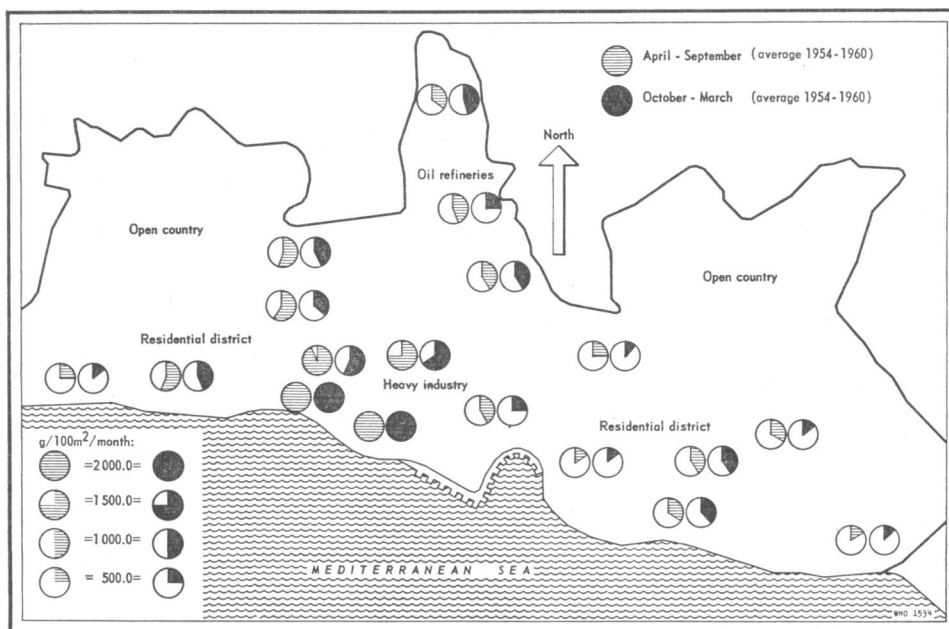


FIG. 5

COMBUSTIBLE MATTER DEPOSITED IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY BRITISH STANDARD DEPOSIT GAUGE ($\text{g}/100 \text{ m}^2/\text{month}$)

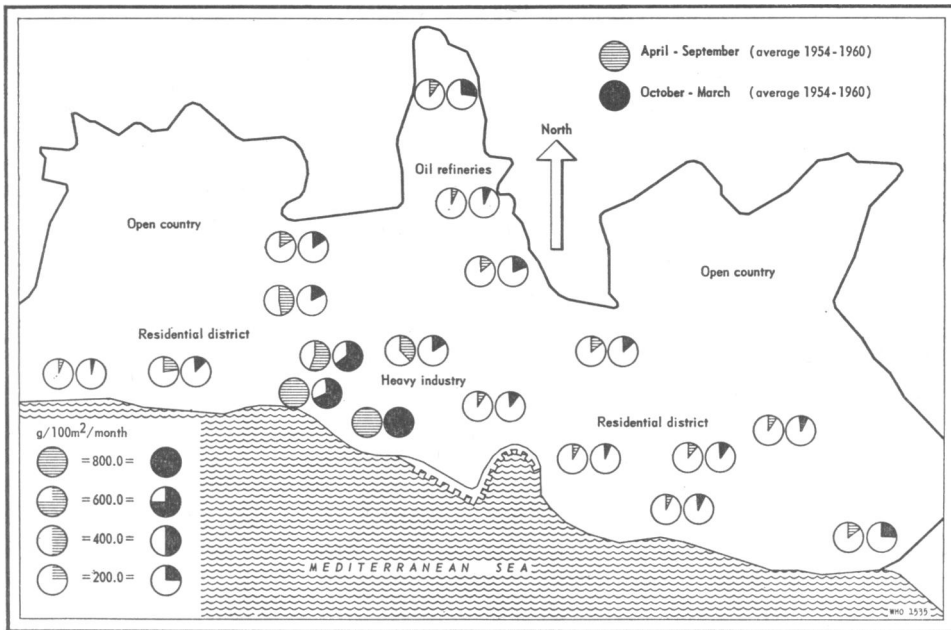


FIG. 6

IRON (Fe_2) DEPOSITED IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY BRITISH STANDARD DEPOSIT GAUGE ($\text{g}/100 \text{ m}^2/\text{month}$)

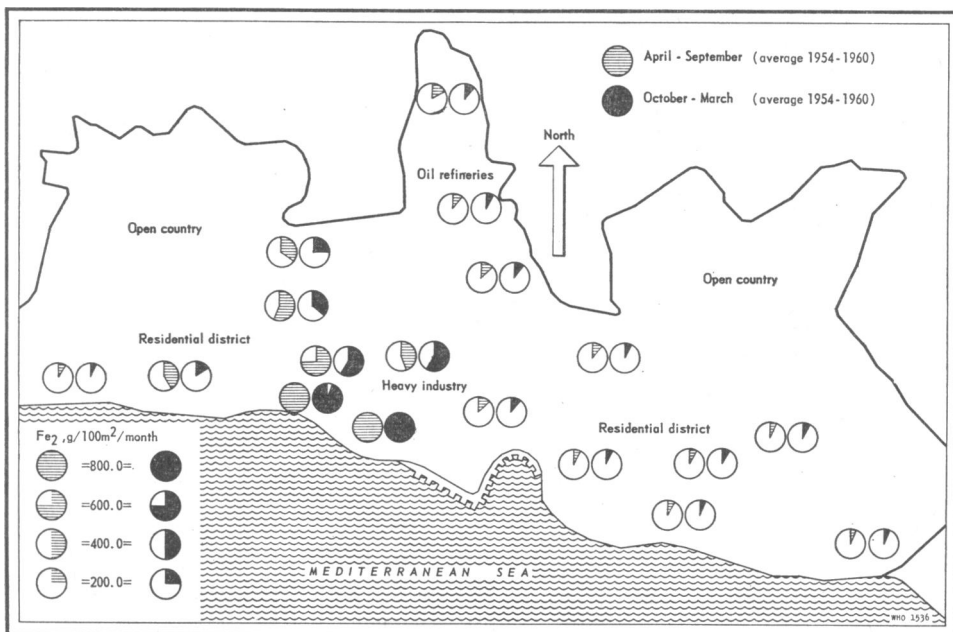


TABLE 11
DUSTFALL COLLECTED BY TWO PAIRS OF DIFFERENT DEPOSIT GAUGES:
AVERAGE VALUES FOR A COLLECTING PERIOD OF 24 MONTHS (1958-1959)
(g/100 m²/month)

Dustfall collected	Zone A			Zone B		
	DSIR deposit gauge	Genoa deposit gauge	Ratio Genoa/DSIR	DSIR deposit gauge	Genoa deposit gauge	Ratio Genoa/DSIR
Total insoluble matter	957	1526	1.59	478	1145	2.40
Ash	644	878	1.36	372	752	2.02
Combustible matter	312	647	2.07	105	393	3.74
Iron (Fe ₂)	337	366	1.09	178	370	2.08
Total soluble matter	326	564	1.73	264	512	1.94
Total dustfall	1283	2090	1.63	743	1658	2.23

smaller than that of the British gauge, prevents the entrance of rainwater in quantities greater than the capacity of the gauge (about 5000 ml), so that the collecting bottles do not have to be changed frequently during the rainy months (in Genoa 6-8 months every year), as in the case of the British deposit gauges.

Table 11 shows an example of the results obtained during a comparison of the quantity of matter collected by the British standard deposit gauge and that collected by the Genoa type in two different districts. The figures represent averages for a collecting period of 24 months (1958-59). It is evident that the Genoa type gauge, despite its smaller

collecting aperture, registers remarkably greater quantities of dustfall. Some careful research was done to discover the real reason for the divergence shown by the two devices.

To this end two pairs of gauges (a British and a Genoa one) were located 500 m away from each other in an area liable to pollution from industrial sources, and for 14 months these were regularly used for collecting dustfall. The data collected (after logarithmic transformation) were submitted to an analysis of variance, with the results shown in Table 12. The significance of the individual variances was submitted to Snedecor's "F" test.

TABLE 12
ANALYSIS OF VARIANCE OF DATA REPORTED IN TABLE 11
(AFTER LOGARITHMIC TRANSFORMATION)

Source of variation	Soluble matter		Insoluble matter		Total matter	
	s ²	P	s ²	P	s ²	P
Between types of gauge	1.179	<0.01	0.971	<0.01	1.064	<0.01
Between months	1.799	0.01-0.05	2.717	<0.01	1.752	<0.01
Between sites	0.109	>0.05	0.683	<0.01	0.440	<0.01
Interaction "types/months"	1.605	0.01-0.05	0.594	0.01-0.05	0.630	0.01-0.05
Interaction "sites/months"	0.318	>0.05	0.283	>0.05	0.194	>0.05
Interaction "types/sites"	0.106	>0.05	0.108	<0.01	0.102	0.01-0.05

The data recorded indicate that:

(1) The results for all the different substances collected differ significantly according to the type of gauge used.

(2) The interactions between types of gauge and months and between types of gauge and areas appear to be significant in respect of insoluble matter and total deposited matter. Practically speaking, this means that the differences observed in collecting these two types of matter with the two types of gauge are not constant, but vary significantly according to the month and area where they were recorded. The variations between the two areas according to the different months are not significant.

(3) Only the interaction between types of gauge and months appeared to be worth considering in relation to soluble matter, apparently in coincidence with the fact that, for these substances, variations between areas are not significant.

The conclusions that may be drawn are that the two types of deposit gauge furnish data which differ quantitatively, the Genoa gauge generally giving higher figures, though the difference is variable. In fact, where the degree of pollution differs according to the area or month of collection, the difference in the effect on the two types of deposit gauge (causing them to measure the dustfall differently) may be significantly greater than that to be expected from sampling errors. Without going into these interesting phenomena in detail, they can be said to confirm the hypothesis that quantitative difference between the results of the two gauges varies under different conditions.

Another aspect from which comparison of the two types of deposit gauge was important before any favourable conclusion could be drawn about the Genoa type under test was the reliability of the results. The manner in which the problem was posed is dealt with further on. Here, attention is merely drawn to the fact that no differences could be found in this respect. The experimental error, considered as residual variance, has been found to be equal to 0.0209 for the British standard deposit gauge used in Genoa, and to 0.0204 for the Genoa type gauge (logarithmic scale).

The latter gauge is at present also used in Genoa as part of an automatic directional sampler constructed by the Institute and used over a long period. This apparatus permits not only the collection of dustfall, but simultaneously that of suspended matter and of one or more gaseous pollutants. It

collects samples for the analyst, which are assessed according to the four prevailing directions of the wind and to wind speed in the polluted area. It consists, in outline, of a central part (five Genoa type deposit gauges, with wind speed and direction measuring devices) to which several apparatuses for sampling suspended matter and gaseous pollutants can be connected. An anemometer electrically operates the opening of one gauge only, according to the direction from which the wind is blowing, initiating operation of the filtration and absorption apparatuses, which receive suspended matter and gaseous pollutants, respectively, diffused from the direction of the wind. When the wind drops, a fifth group of samplers comes into operation. This type of apparatus is useful for studying the behaviour of gaseous and solid pollutants in air movements. It must, of course, be used simultaneously with an anemograph.

As the pollution by iron dust particles is of particular interest in Genoa, a simple, practical method has been adopted which can be used also for suspended matter and can measure variations in the concentration of particles in the air. The sampling method consists in exposure to the air of Petri dishes, covered on the bottom with a thin layer of agar-agar or any other suitable jelly free of iron. After exposure (from 10 seconds to 10 minutes) the collecting surface is treated with a potassium ferrocyanide solution (0.1%) in diluted hydrochloric acid (1:5). After a short time (5 minutes), the iron particles are easily recognized by their characteristic blue halo and can be counted. Table 13 gives, as an

TABLE 13
MEASUREMENTS OF SETTLING IRON PARTICLES IN
GENOA

Site	Number of particles (Fe+++ /m ² /hr)	
	Minimum	Maximum
Residential district	4	50
" "	5	38
" "	4	26
" "	9	15
Heavily industrialized district	138	850
" " "	275	1350
" " "	86	1650
" " "	465	970
Oil refinery district	15	55
" " "	14	32
" " "	23	39

example, the minimum and maximum figures for a sampling series of sedimenting iron particles recently made (August 1960) by the method described above, all within two hours of each other, in various parts of Genoa.

SUSPENDED MATTER

Matter suspended in the air may be composed of liquid droplets and solid particles. Usually, the term "suspended matter" implies either solid particles or "smoke", which is, of course, composed of both.

Of the three components of air pollution considered in this paper, suspended matter is undoubtedly the one for which practically no standard measurements exist. Research done in Italy relates to suspended matter as a whole and the quantity and size of its particles. The data at present available for this type of pollution cannot be compared quantitatively with those for sulfur dioxide and dustfall. Nor are there many qualitative data on suspended matter in Italy. Those that do exist derive from non-routine research—for example, the measurement of lead from motor-traffic exhausts, the measurement of arsenic, studies on fuel combustion and on substances suspected of carcinogenic action, and the measurement of atmospheric radioactivity.

The most common method of measuring suspended matter is by means of drawing a measured volume of air through a paper filter. The evaluation is made either by comparing the degree of blackness of the sample with a standard scale of shades, or, when using weighed filters, by weighing the samples (see Table 14 and Fig. 7).

Besides apparatus of the volumetric type, which holds a paper filter between the air-sample entrance and the gas-washing bottle, some portable high velocity samplers are also used for filtration and are able within a short period (one hour) to collect samples of a volume ample enough to be representative. To evaluate the quantity and size of the dust particles, several techniques are available, such as Owen's dust-sampler, different konimeters (Zeiss, Sartorius, etc.), various kinds of impinger, the Watson-Green thermal precipitator, the electrostatic precipitator, etc. The size of the particles is measured by counting them with a light-field, dark-field or phase-contrast microscope.

In Genoa automatic continuous samplers have been in use for a long time and some results have already been published. The advantages are obvious

TABLE 14
SUSPENDED MATTER IN GENOA (1956-1960) :
MEASUREMENTS AT 18 SITES BY THE GRAVIMETRIC
METHOD EMPLOYING MEMBRANE FILTER SAMPLERS

Site of instrument	Summer (mg/m ³)	Winter (mg/m ³)
1	0.13	0.20
2	0.14	0.22
3	0.09	0.16
4	0.25	0.45
5	0.26	0.47
6	0.20	0.30
7	0.20	0.40
8	0.85	0.66
9	0.98	0.57
10	0.05	0.08
11	0.15	0.23
12	0.12	0.19
13	0.10	0.18
14	0.15	0.20
15	0.29	0.25
16	0.28	0.32
17	0.26	0.45
18	0.04	0.07

if only because this technique enables variations in suspended matter to be measured from hour to hour without interruption for days, months or years, with only a minimum of maintenance. Evaluation of the results is done by a special "densitometer", which measures the light transmission of samples. The quantity of "smoke" darkening the filter is expressed in conventional units, such as units of optical density/cm²/m³. We also use a sampler which permits the collection of different samples on various membrane filters according to the direction and speed of the wind. This last apparatus, as already mentioned, is used simultaneously with the directional dustfall sampler.

Among the usual methods of evaluating the quantity and size of dust particles, observation by electron microscope must be mentioned. In this case we usually use samples collected by the thermal precipitator or by membrane filters. This technique can help to clarify interesting points regarding the structure and aggregation qualities of the minutest

FIG. 7
SUSPENDED MATTER IN GENOA (1954-1960) : MEASUREMENTS AT 18 SITES BY HIGH-VOLUME SAMPLERS
(mg/m³)

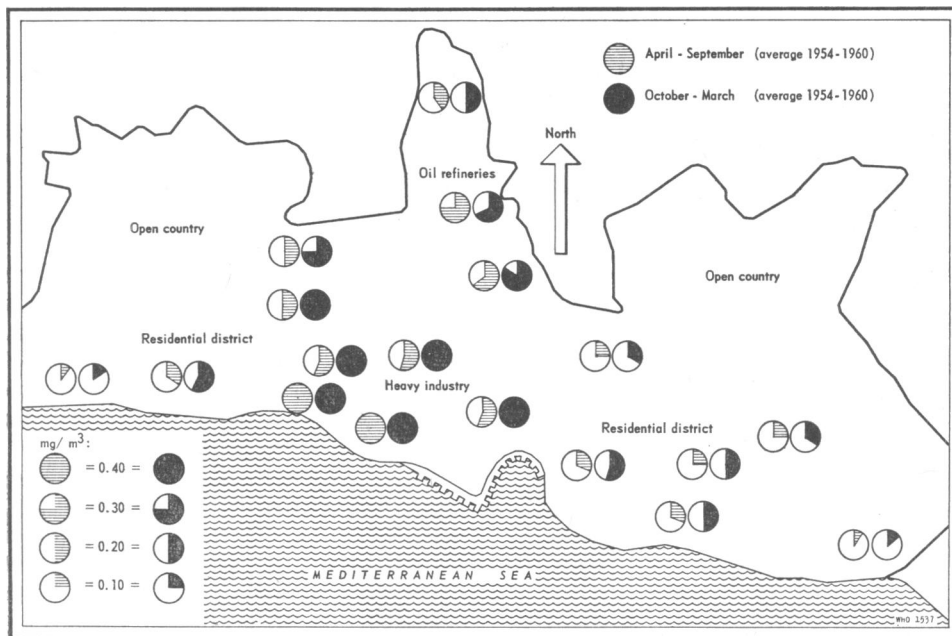
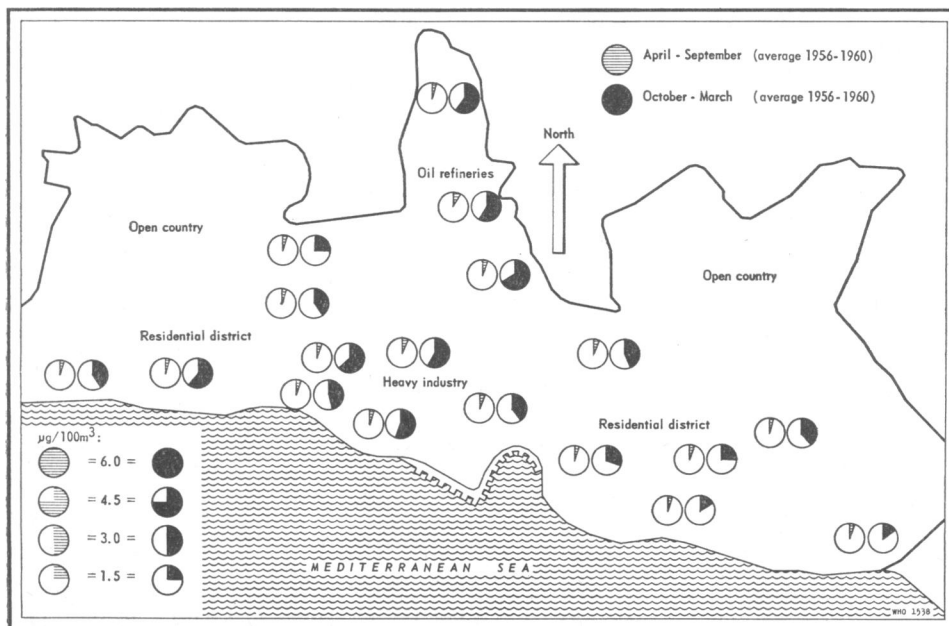


FIG. 8
3,4-BENZPYRENE IN SUSPENDED MATTER IN GENOA (1956-1960) : MEASUREMENTS AT 18 SITES BY MEMBRANE FILTER
SAMPLERS (μg/100 m³)



particles. This is a matter of the utmost importance to a better understanding of the effects of air pollution on the human organism. For example, the structure of dust formed mainly by iron, manganese, and silicon oxides emitted by electric furnaces appears to be very different from that of dusts from other industrial installations.

In this field research is being carried out on the identification of particular types of dust particle in thin sections of the lung tissues of animals in certain areas of Genoa or exposed to inhalation experiments in the laboratory. As already mentioned, investigation of substances suspected of carcinogenic action in the suspended matter from certain areas of the city is being pursued. The samples for this study are collected by filtering large volumes of air through special membrane filters and sampling known volumes of air through special traps (three in a series) for condensing the pollutants at very low temperatures (-60°C to -80°C) (see Table 15 and Fig. 8). The analytical methods used are, with some modifica-

tions, those followed by British workers—i.e., chromatography on alumina columns and absorption-spectrophotometry of specific hydrocarbons. Among the principal substances of this type for which we are searching are: 3,4-benzpyrene, 1,12-benzperylene, coronene, anthracene, fluorene and pyrene. Finally, it should be mentioned that a search is being conducted for these suspected carcinogenic substances from suspended matter in the air filters of motor cars, since it has been observed in Genoa that mortality from lung cancer is significantly higher among car drivers.

Of all the above-mentioned methods, the use of automatic samplers to study variations in concentrations of suspended matter seems of particular interest to the writer. The number and size of particles can be usefully determined by collecting samples on membrane filters. The method also facilitates any form of microscopic observation.

Where large-scale sampling is concerned, the writer believes that the simple konimeter has been set aside too soon, as this instrument does permit a large number of samples to be collected and evaluated in a few minutes. While there must be reservations about the validity of dust sampling by impingement, there is no doubt that the data supplied by the konimeter are very useful for practical purposes in a preliminary survey. They can help in deciding, for example, the size and frequency of samplings required by other techniques (thermal precipitator, collection on membrane filters, etc.) for being in the best condition when the samples have to be analysed in the laboratory and examined under the electron microscope. For these reasons the konimeter should not be neglected when it comes to standardizing the different methods.

In selecting methods for evaluating the total suspended matter and also for counting and measuring dust particles, more than in the case of other pollutants, a study of standardization is urgently required. This might be undertaken at an international level by a restricted expert committee, each expert having at his disposal the methods considered more suitable for standardization and for analysing the results obtained by reliable statistical methods.

One aspect of the problem of air pollution measurement given particular attention in Genoa is the reliability of different techniques. Bearing in mind the epidemiological purpose of this research—i.e., to determine whether there is some relation between air pollution and human health by comparing the measured differences in air pollution with

TABLE 15
3-4 BENZPYRENE IN SUSPENDED MATTER IN GENOA
(1956-1960) : MEASUREMENTS AT 18 SITES BY MEMBRANE
FILTER SAMPLERS

Site of Instrument	Summer ($\mu\text{g}/100 \text{ m}^3$)	Winter ($\mu\text{g}/100 \text{ m}^3$)
1	0.25	1.62
2	0.15	1.58
3	0.26	2.72
4	0.18	3.21
5	0.05	3.86
6	0.16	1.54
7	0.37	2.45
8	0.27	2.96
9	0.21	3.16
10	0.10	2.79
11	0.46	3.81
12	0.28	2.61
13	0.18	2.64
14	0.09	3.68
15	0.14	3.46
16	0.10	4.09
17	0.12	3.88
18	0.18	1.22

health indices—it is important to pin-point certain factors in the problem. It must not be forgotten that one can be led to incorrect conclusions by three types of error:

- (1) errors in the measurement of health conditions (very easily committed);
- (2) errors in the method of comparison;
- (3) errors in the measurement of the air pollution.

The last-mentioned, in this particular case, are probably the least important and most easily set right (in the relative sense), but for this very reason they should not be neglected. In other words, our goal is to make sure that the differences in air pollution, in part at least, are beyond discussion when the comparison between variations in air pollution and health indices appear to indicate some relation between the two phenomena. Following a series of measurements of dustfall by means of two types of deposit gauge (the British standard and a Genoa type) over the past few years, we tried to observe whether the data which we had collected could be used to evaluate the sampling error inherent in the method employed and, consequently, establish some general rules about the results available from different sampling methods. Thus, we have assembled some readings collected between 1957 and 1959 and by an analysis of variance have estimated the so-called residual variance (discrepancy, error) representing that part of all deviations from the general mean that cannot be related to actual differences among the existing air pollution levels, but arises exclusively from the sum of the experimental errors of measurement. An estimate of the experimental error obtained by this method can, of course, express the errors not only characteristic of the sampling method, but also due to acci-

dental factors which do occasionally occur in specific cases and which are not covered by separate calculations, as in the case of the two sources of factor variations, "months" and "sampling site".

However, where it is possible to show that the residual variance is constant on different occasions there are grounds for thinking that a really basic error is involved, repeating itself constantly each time the measurement is made according to the prescribed rules. This is then the experimental error, characteristic of the sampling method employed.

The results obtained by our calculations are given in Table 16. These data show that, while the figures for variance "between areas of sampling" and "between months" vary from one experiment to another, those for the "residual variance" are very similar to each other, with small deviations from 0.02. After checking that there is no significant difference between the five residual variances (s^2) obtained, it can be calculated that:

for average British standard deposit gauges	$s^2=0.0209$	$n=99$
for average Genoa type standard deposit gauges	$s^2=0.0204$	$n=123$
for average standard deposit gauges, both types	$s^2=0.0206$	$n=222$

The practical significance of the "experimental error" figures is that when a sample equal to 100 is determined by means of a deposit gauge of either the British or the Genoa type, this figure must be understood as an estimate of the true value of the existing degree of pollution within the following fiducial limits:

$P=0.05$	52-193
$P=0.01$	43-233

TABLE 16
DUSTFALL COLLECTION BY TWO DIFFERENT TYPES OF DEPOSIT GAUGES
IN DIFFERENT AREAS OF GENOA (1957-1959): ANALYSIS OF VARIANCE OF THE DATA
(AFTER LOGARITHMIC TRANSFORMATION)

Source of variation	Deposit gauges, British type		Deposit gauges, Genoa type		
	1957	1958	1957	1958	1959
Between areas	1.4407	1.0970	0.5377	0.9568	0.6240
Between months	0.2686	0.3555	0.4393	0.1168	0.0977
Experimental error	0.0217	0.0203	0.0294	0.0195	0.0187

TABLE 17
DUSTFALL COLLECTION IN GENOA:
SIGNIFICANT DIFFERENCES ACCORDING TO NUMBER
OF GAUGES EMPLOYED

Number of gauges	Significant difference ($P=0.05$)
1	100-253
2	100-193
3	100-171
5	100-151
10	100-134

The data in Table 17 make it possible to calculate the significance of any possible differences according to the number of gauges used for measurement.

After examining the experimental error in measurements of sedimented matter, we applied the same statistical calculations to data from the other analysis of material collected by deposit gauges. The results are shown in Table 18. The determination with the minimum of error was that for soluble matter, while for insoluble matter the combustible fraction is the one for which the data are relatively more accurate. Experimental error in measurement of ash and iron (Fe_2) is the greatest.

It is not easy to explain these differences satisfactorily. Generally speaking, after concluding that they cannot depend on the different absolute values of the data (this possibility is excluded by the use of logarithms), it may be supposed that the different sizes of dust particles, the different rates of settle-

TABLE 18
ESTIMATES OF THE EXPERIMENTAL ERROR
IN MEASURING DUSTFALL IN GENOA: ANALYSIS
OF VARIANCE AFTER LOGARITHMIC TRANSFORMATION

Dustfall collected	Experimental error	95% fiducial limits of a sample equal to 100
Total dustfall	0.0206	52-193
Soluble matter	0.0133	88-160
Insoluble matter	0.0235	49-202
Combustibles	0.0305	45-223
Ash	0.0724	29-345
Iron (Fe_2)	0.0916	25-402

ment and the varying degree to which the particles are affected by meteorological factors have an influence.

There are not many points of reference for comparison of our data with those of other research workers. Craxford, Slimming & Wilkins,¹ supported by data collected in England by using pairs of adjacent deposit gauges, conclude that for practical purposes individual readings of insoluble matter have an accuracy of about $\pm 20\%$. If we express our data in this form, we find a rather greater variation for insoluble matter, of the order of 40% . This difference, in the opinion of the above-mentioned authors, can be explained by the fact that the readings made in Genoa are in areas which are relatively nearer to air pollution sources and also by the different topographic and meteorological characteristics of the two countries. The same type of analysis of experimental error has been made for measurements of sulfur dioxide by the lead-peroxide apparatus, using a total of 408 monthly recordings collected between 1957 and 1959 in different areas of the town of Genoa.

The analysis of variance was calculated on the data before and after logarithmic transformation. In the first place it was observed that the experimental error was not proportional to the absolute value of the general mean of the data, but was, on the contrary, more easily established and more constant when the data were calculated arithmetically. Table 19 gives the results of these calculations.

Using Bartlett's test of homogeneity of variance on the experimental error values (residual variance), we have found that:

$$\chi^2=6.78; \quad n=5; \quad P>0.05$$

The weighted mean of experimental error values:

$$s^2=0.04 \quad (n=308)$$

can be taken as a reliable estimate of the experimental error which is characteristic of the measuring technique. It follows, therefore, that $s = 0.20 = \sigma$. The fiducial limits (at 95% confidence interval) are of the order of ± 0.40 . As already stated, these limits would have to be considered independent of the absolute sulfur dioxide readings, and for this reason proportionally larger when the concentration measured is lower.

¹ Craxford, S. R., Slimming, D. W. & Wilkins, E. T. (1960) *The measurement of atmospheric pollution: the accuracy of the instruments and the significance of the results*. In: National Society for Clean Air, *Proceedings of the Harrogate Conference, 1960*, London.

TABLE 19
ANALYSIS OF VARIANCE OF THE RESULTS OF SULFUR DIOXIDE MEASUREMENT
BY LEAD-PEROXIDE APPARATUS IN GENOA

Source of variation	Residential districts			Industrial districts		
	1957	1958	1959	1957	1958	1959
Between areas	0.6215	0.7500	0.9725	0.4983	0.4083	0.3150
Between months	0.2945	0.2000	0.4909	0.3190	0.1572	0.3381
Experimental error	0.0361	0.0631	0.0384	0.0412	0.0469	0.0321
Average SO ₂ (mg/100 cm ² /day)	0.36	0.43	0.43	0.98	1.03	0.92

The experimental error we have calculated is rather large, both absolutely and relatively. Where only two readings are compared, it is possible to consider only one difference of 0.56 mg/100 cm²/day (or greater than this) as significant.

The variability found in Genoa appears to be greater than that found in London and Thornton-hall by Craxford et al. This last observation is interesting in that it draws attention to the relative suitability of a measuring method for the characteristics of the area to be examined. For instance, measurement by a lead-peroxide apparatus may be influenced by a factor, such as the speed of the wind, which during the autumn and winter season is particularly high and variable in Genoa, and bearing this in mind one can understand the differences observed.

In conclusion, it would seem that a systematic study of the experimental error characteristic of each method employed by different research workers in the various areas is highly desirable, not only for a more precise evaluation of individual results, but also for determining whether certain methods are reliable, here, for obtaining standardized results.

So far, different methods and apparatus for the measurement of air pollution have been dealt with. It should be added, however, that a static network of measurement stations is not enough. This network must be integrated with a mobile laboratory, supplied with all the proper apparatus for measuring also pollution situations that arise suddenly or are of a brief duration. At the same time, the possibility thus offered of making on-the-spot observations and analysis should not be neglected. In Genoa a laboratory mounted on a truck is used, allowing the

measurement of sulfur dioxide (with the autometer, CEGB apparatus, and so on), of other gaseous pollutants and of suspended matter. It is provided with a portable anemograph and other meteorological instruments.

There is no need to emphasize the importance of the simultaneous measurement of meteorological factors and air pollutants. In this connexion it should be said that the relations between meteorological conditions and air pollution which we are studying are, above all, characterized by their complexity. Indeed, it has been observed that different factors are suspected of exerting a varying degree of influence depending on the circumstances and types of pollution under consideration.

The simultaneous intervention of several factors represents practically the greatest difficulty encountered in seeking to establish at all accurately which individual meteorological factors are of actual importance, and to what extent. Suitable methods of statistical evaluation must be adopted to overcome this difficulty. In Genoa multiple and partial correlation and multiple and partial regression have been used, for instance, to examine the relations between dustfall and some of the more frequently considered meteorological factors: direction and speed of the wind, rainfall (in millimetres), number of rainy days, humidity, temperature and air pressure. Some of the results arrived at are shown in Table 20.

The variances imputable to the three partial regressions are significantly superior to those ascribable to the deviations from the regression. The anemological conditions, therefore (wind above 20 km/hr), responsible for 49% of the deviations, the air humidity for 28% of the deviations, and the

TABLE 20
REGRESSION OF AIR POLLUTION (DUSTFALL) ON SOME METEOROLOGICAL
FACTORS: ANALYSIS OF VARIANCE

Source of variation	Sum of squares	Degrees of freedom (n)	Mean square (s ²)	F	P
Multiple regression $x/y_{1,37}$	90 855	3			
Partial regression $x/y_{1,37}$	23 582	1	23 582	17.11	<0.01
Partial regression $x/y_{3,17}$	8 772	1	8 772	6.36	0.01-0.02
Partial regression $x/y_{7,13}$	17 950	1	17 950	13.02	<0.01
Error	77 217	56	1 378		
Total	168 072	59			

y = Air pollution (deposit gauges).

x_1 = Wind above 20 km/h.

x_3 = Humidity.

x_7 = Frequency of consecutive days without rain.

frequency of consecutive days without rain for 23% of the deviations, have been found to be correlated with the air pollution (dustfall).

These results, apart from their incidental value,

seem worth mentioning, as they show that the use of statistical methods that bring out the simultaneous influence of several factors lead to findings of evident practical interest.

RÉSUMÉ

Depuis 1954, il est procédé en Italie à l'étude des trois polluants principaux que l'on rencontre dans l'atmosphère des villes: l'anhydride sulfureux, les poussières, et les « matières en suspension », c'est-à-dire les particules solides ou la fumée. Le présent article analyse les résultats obtenus à Gênes, de 1954 à 1960, au moyen d'instruments de mesure et selon des méthodes qui font l'objet d'une description détaillée et d'une évaluation critique.

Afin d'obtenir d'emblée des données autant que possible uniformisées, divers dispositifs de conception britannique (*Department of Scientific and Industrial Research*) ont été utilisés. La réaction au peroxyde de plomb, le plus souvent employée pour le dosage de l'anhydride sulfureux, est un procédé pratique qui donne des résultats satisfaisants; il peut cependant être utilement complété par l'enregistrement continu et automatique des concentrations en SO_2 (automètre Thomas modifié), surtout dans les limites d'application habituelles (0 à 5 p.p.m.). Sensible à des concentrations de 0,05 p.p.m., cet appareil enregistreur décèle des augmentations soudaines et passagères de SO_2 qui peuvent éventuellement exercer des effets physiologiques.

Les poussières atmosphériques ont été mesurées soit avec l'indicateur de retombée mis au point et standardisé

par le *DSIR*, soit avec un appareil de construction génoise, dérivé du précédent. Ce dernier est d'un manie-ment plus simple et plus économique, mais sous l'effet de diverses conditions météorologiques (vent, pluie, etc.), les données de ces deux instruments présentent des écarts importants. Ce fait indique la nécessité urgente d'une standardisation dans les techniques de construction et d'emploi des instruments, ainsi que dans la lecture des résultats, si l'on veut disposer de statistiques comparables et échanger des informations.

Cela est vrai plus encore de l'analyse des matières en suspension pour laquelle aucun accord de méthode n'est encore réalisé. A côté de la technique ancienne qui consiste à faire passer sur différents milieux un volume d'air déterminé, on utilise en Italie les précipitateurs thermique ou électrostatique, et des conimètres de divers types. Il est à noter cependant que, pour les matières insolubles, la précision des dosages n'est que de $\pm 20\%$, et même $\pm 40\%$. A Gênes, il a été procédé également au filtrage automatique sur papier et à la numération des particules sur membranes filtrantes. L'examen au microscope électronique des particules recueillies, et le dosage des polluants éventuellement cancérogènes pour l'homme, ont ouvert la voie à des recherches prometteuses.