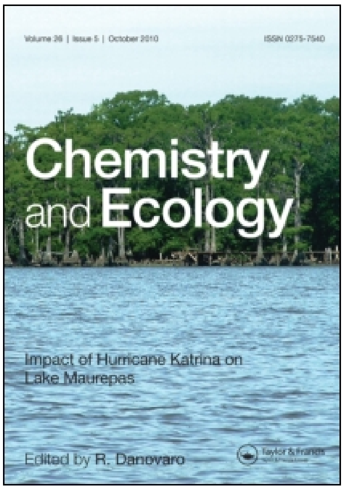

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ASSESSMENT OF THE WATER QUALITY OF THE RIVER ARNO IN THE AREA OF FLORENCE, ITALY

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The quality of the waters collected from R. Arno was examined in the period September 1988 to December 1989. A first campaign in September/October 1988, during a period of low water, gives a general picture of pollution conditions along the river from the source to the mouth. The river appears to be heavily polluted immediately downstream of Florence and in the area of the textile industry.

In the second campaign, through the whole year 1989, particular attention has been given to the Florence area; the most significant results, compared with those from a previous investigation carried out in 1971, show only a small reduction of the pollution load, due to the shortage and inadequacy of wastewater depuration. Some considerations are reported on pollution drop with full spate.

KEY WORDS water quality, river pollution, Florence area

INTRODUCTION

The river Arno is one of the largest Italian rivers; its catchment of approx. 8200 km^2 is wholly situated in the Tuscan area, in central Italy. The whole of the Arno valley abounds in urban settlements (mainly the towns of Arezzo, Pisa and Florence) and in usually small-scale factories. The area has an important historical and artistic background, pleasant countryside and fertile land which is used for high-quality agriculture. Today, however, the whole valley is threatened by a high degree of water pollution which is difficult to control because of the widespread nature of the sources of this pollution.

Investigations into the state of pollution of the Arno have been carried out since the mid-seventies (Santopadre and Lapucci, 1963; Lapucci *et al.*, 1967; Signorini and Grasso, 1965). These studies identified critical reaches where pollution reached its maximum, already then considered intolerable, levels, as being near the city of Florence and immediately downstream. A large body of observations appears in the pollution maps charted by the public authorities (Regione Toscana, 1974; 1976; Associazione Intercomunale Area Fiorentina, 1987), and investigations directed more specifically at the geographical area near in water (UK-DoE, 1979; UK-DoE, 1986 and ECETOC, 1988), but it has been difficult to attribute these effects to fertilizer use alone. Much of the early work on this subject indicated that land use or agriculture practice, rather than fertilizer use, were the major factors influencing nitrate loss to surface water (Haith, 1976; Haith and Dougherty, 1976). Various studies have examined the relationship between the land use and nitrate concentrations in isolated watersheds (Klepper, 1978; Edwards *et al.*, 1990). There are, however, within the UK, few studies on a regional scale (SSLRC/ITE, 1989) capable of elucidating the relationship between land cover (agricultural intensity) and water quality.

The purpose of this paper is to report an integrated study of conventional chemical river catchment analysis, and agricultural census returns, together with a computer technique for the manipulation of spatial geographic information (GIS) to investigate this problem. Computer manipulation of spatial map images allows the areal breakdown of land attributes within individual river catchments and sub-catchments.

NITROGEN AND AGRICULTURE

The relationship between leached nitrate and nitrogen applied is not straightforward. Soils contain substantial amounts of organically bound nitrogen. A number of factors affect the rate of release of nitrate from these organic sources and include soil type, temperature, moisture and management practices (Low, 1976; Jenkinson, 1982 and 1986). Additional inputs of nitrogen from atmospheric deposition and biological N fixation can also make significant contributions to the overall N budgets of natural ecosystems.

In general terms, the amount of nitrate leached from the soil is dependent on three main factors (UK-DoE, 1979). First, the water balance between rainfall received at a site, water lost in evapotranspiration from vegetation cover and the water holding capacity of the soil. Secondly, the quantity of nitrogen present in the soil either from natural sources or fertilizer input. Finally, the degree to which nitrogen is removed by the vegetation cover present at the site.

The importance of any single source of nitrogen will vary considerably over the study area. Aspects of the nitrogen cycle in the United Kingdom have recently been reviewed, atmospheric deposition (taken as 20 kg N/ha-yr) making a particularly important contribution to the overall nitrogen budget of upland areas (Batey, 1982). The importance of such variables as land cover and soil type on the potential for NO_3-N leaching is by no means clearly established (Ryden *et al.*, 1984; Gasser, 1982 and Kolenbrander, 1983). Nitrate leaching increases as land use changes from moorland through forest, and grassland to arable agriculture. It also varies with season, disturbance and site characteristics. In an individual heather or moorland plant community, there is a very little nitrate loss, of the order of 1 or 2 kg NO_3-N per ha-yr (Edwards *et al.*, 1985). Stevens and Hornung (1988) found that nitrate leaching could increase by six to ten times following clear felling of forestry.

On arable soils the greatest leaching losses occur during late autumn, winter and early spring following periods of reduced plant uptake, increased tillage and incomplete ground cover to intercept the nitrate released by mineralization or fertilizer application. During this time rainfall exceeds moisture losses by evaporation and transpiration. Arable land loses one third and grassland one tenth of the amount of nitrogen lost by fallow land into the drainage system (Low and

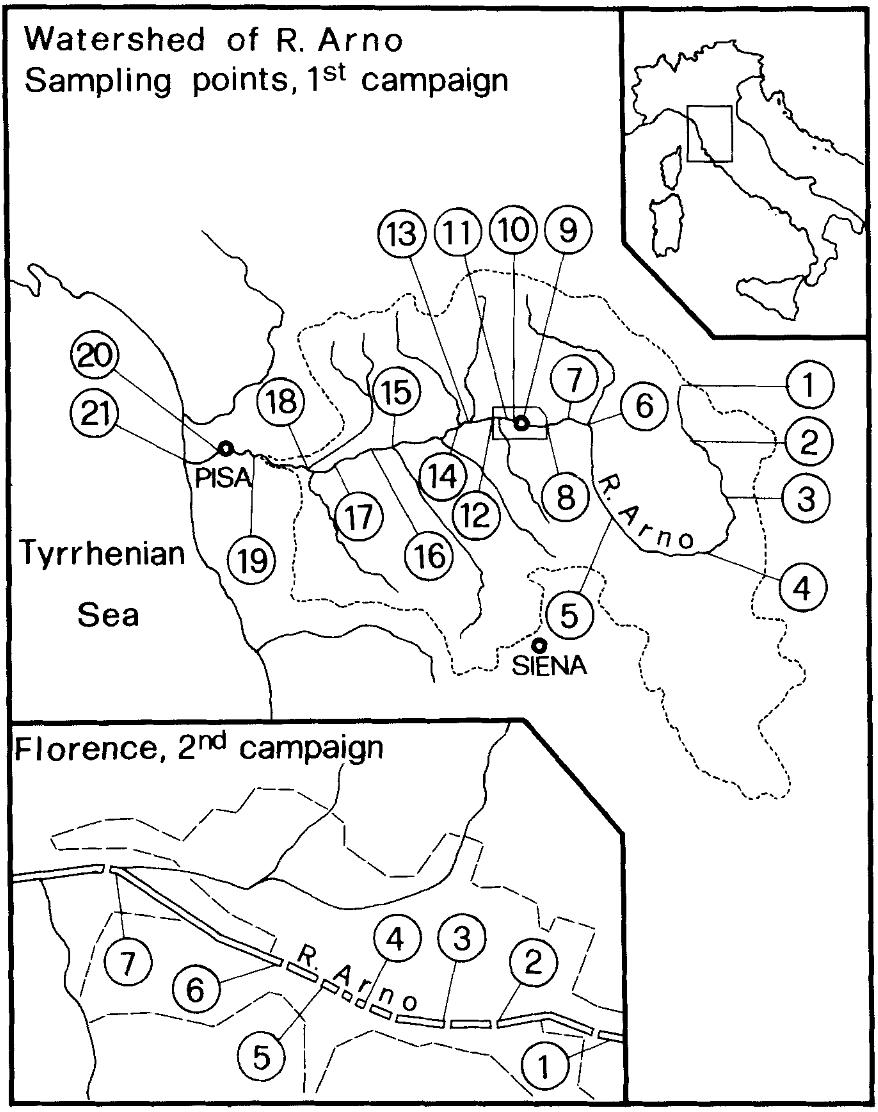

Figure 1 Map of the sampling points along the R. Arno in the first campaign and in the Florence area in the second campaign.

areas of Florence, where over 500,000 inhabitants live and work. In this area there is practically no sewage treatment. After a few kilometres the river Arno receives the wastes from the area of Prato, a large textile-producing centre. The inhabitant equivalents of discharges in this area are >1,000,000 and the sewage is only partially treated. The COD reaches its highest values at these locations. Further downstream, the Arno flows through the area of Santa Croce, which is particularly rich in tanneries. This industrial area recently installed a large treatment plant with a capacity to treat wastes of approx. 3,000,000 inhabitant

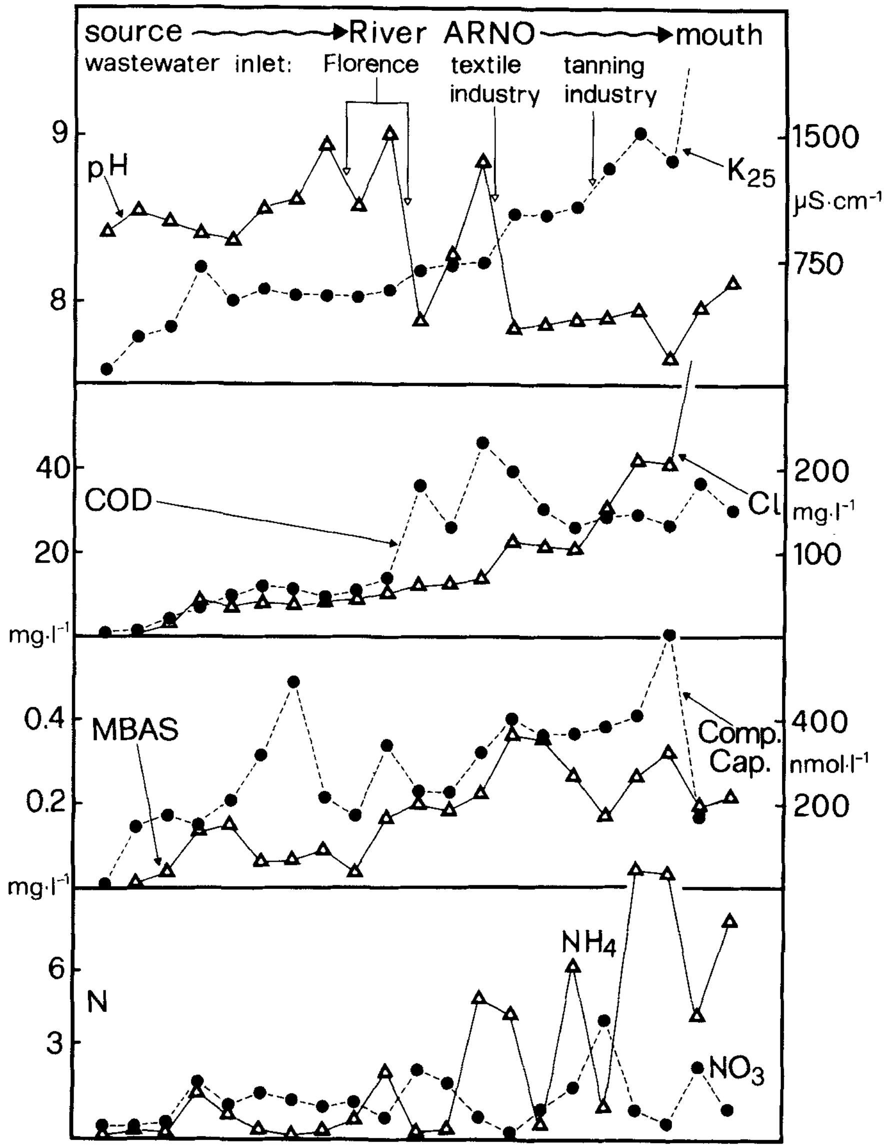

Figure 2 Values of the water quality constituents determined along the course of R. Arno during the campaign in Autumn 1988.

equivalents. The pollution level of the river, as mainly indicated by COD, which is already very high upstream of the treatment plant, is not increased. Still further downstream, near the mouth, the conditions of the river are no longer affected by discharges but rather by the ebb and flow of the tides.

The overall salt content, as indicated by the electrical conductivity value, gradually increases as the river proceeds to its mouth. The pH values upstream of Florence are approx. pH = 8.5, typical of relatively unpolluted surface waters; in the last section of the river the values are constantly below 8, as usual for a river that receives numerous sewage discharges. The values reported for the middle reaches, where the largest discharges occur, are considered to be widely variable when sampled in different periods.

A variable that is usually highly indicative of pollution from domestic sources are the anionic surfactants, usually determined as Methylene Blue Active Substances (MBAS). The highest values are found where the river passes through very built-up areas. However, the maximum values immediately observed below the sewage discharge from the Prato area are indicative of the great use made of these products by the textile industry there. The two nitrogen forms, nitrate and ammonia, seem to be inversely correlated to each other. In the section of river with low pollution nitrate nitrogen is seen to prevail over ammonia nitrogen, while the opposite is true for the last sampling stations, where the Arno is highly polluted.

Second Campaign

In the second part of this investigation, we concentrated on the section of the river passing through the urban area of Florence. The 7 sampling stations were located as follows:

1—Varlungo, in the suburban area upstream from Florence, at the beginning of the municipal district

2—Verrazzano bridge, an area of recent urban settlement

3—St Niccolò bridge, adjoining the circle of the old city walls

4—Ponte Vecchio (The Old Bridge), in the old city centre

5—Vespucci bridge, in the western part of the old centre

6—Vittoria bridge, an area which has been built up in this century

7—the Indiano area, at the end of the "Cascine" park, a downstream suburban area.

The state of pollution of this urban section of the river was the object of an earlier study (Pantani *et al.*, 1972). Over the last twenty years, the urban area has grown further, incorporating some border districts into a single built-up area. Some treatment plants which have since been installed serve only a few thousands of inhabitants and seem to have little effect on the sewage discharges produced over the whole area. A part of the wastes arising from the area north of Florence, discharged to the Arno at the point where sampling station No. 7 is located, has for some years been diverted to a secondary channel which also flows into the Arno some kilometres further downstream. We report the more general conclusions that may be drawn from observations on differences in water quality values at sites 1 to 7 (mean values, Table 1), and those relative through the year 1989 (Table 2). It is important to note that the period considered was characterised by a certain abnormality of climate for Tuscany, as for the whole of Italy, since the winter 1988/89 and also the following Autumn 1989 were

Table 1 Means of the concentrations of the components in water from R. Arno at the various stations (monthly samples during the year 1989).

	Station						
	1	*2*	*3*	*4*	*5*	*6*	*7*
Cond. K_{20}, $\mu S/cm$	438.4	441.4	439.8	439.2	443.9	451.1	496.0
pH	8.12	8.00	7.95	8.01	8.00	8.03	7.90
Redox Pot., mV	134.6	109.8	118.1	117.8	98.0	115.3	99.6
COD, mg/l	18.1	19.5	18.9	18.5	19.5	19.6	27.8
MBAS, mg/l	0.08	0.10	0.11	0.15	0.11	0.16	0.74
$N-NH_4$, m.equiv/l	0.035	0.041	0.043	0.037	0.043	0.051	0.137
$N-NO_3$, m.equiv/l	0.16	0.16	0.16	0.19	0.18	0.17	0.23
$N-NO_2$, m.equiv/l	0.0039	0.0040	0.0037	0.0036	0.0044	0.0044	0.0066
Ca, m.equiv/l	3.41	3.32	3.29	3.43	3.42	3.39	3.57
Mg, m.equiv/l	0.99	1.02	0.93	0.91	0.81	1.06	0.88
Alkalin., m.equiv/l	3.59	3.56	3.70	3.48	3.54	3.58	3.92
Cl, m.equiv/l	0.96	0.98	1.00	1.01	1.01	1.06	1.24
SO_4, m.equiv/l	1.01	1.01	0.99	1.02	1.00	0.99	1.06
Pb, $\mu g/l$	24.4	16.9	37.0	36.4	21.6	22.8	112.9
Cd, $\mu g/l$	3.21	1.77	1.93	2.89	4.17	2.09	6.50
Zn, $\mu g/l$	29.2	27.1	55.6	27.6	51.5	22.4	39.8
Cu, $\mu g/l$	4.86	6.72	8.22	7.81	7.22	5.27	9.27

extremely dry, just as those periods of the year that are normally rather rainy. In the other periods, though the rainfall events approach the norm, the rains were often brief but intense.

Proceeding downstream, no clear variation can be found in the water quality characteristics of the river for variables that are not indicative of pollution, thus the values given for sulphate, nitrate, alkalinity, alkali metals and alkaline-earth metals may be taken as representative. For variables that typify pollution, i.e. COD, anionic surfactants and ammonia nitrogen, on the other hand, a gradual deterioration of the quality of the water is observed. The last sampling station shows the highest concentrations and thus largest degree of degradation. This results from the various discharges of sewage through the urban area but, in addition, it is at the point of station 7 that a degraded, sewage-carrying tributary (the Mugnone stream) flows into the river.

It is useful to compare the most significant results of the 1972 investigation (Pantani *et al.*, 1972) with those of the present study. The sampling stations then used corresponded to Nos. 2, 4, 6 and 7 of the present investigation. BOD_5 instead of COD findings are available for the earlier study, the latter now being held to be more reliable from the point of view of chemical analysis. In any case in surface waters polluted by domestic sewage it is expected that BOD_5 corresponds to roughly about 70% of the respective COD value, and that the comparison is valid. In Table 3, where some indicative pollution indices are reported, water quality is seen to deteriorate in the same downstream trend as previously.

However, the increase in the pollution indices at the last station (7), downstream from the town, that in the former investigation had appeared huge, is much less today. This can be explained to be due mainly to the fact that the biggest sewage discharge of the urban area has been displaced further down-

Table 2 Means of the concentrations of the various components in water from R. Arno; replicate determinations on samples collected at the dates specified, in the year 1989.

	Date of Sampling								
	Jan 16	*Feb 9*	*Mar 8*	*May 1*	*Jun 21*	*Jul 26*	*Aug 25*	*Oct 4*	*Dec 5*
Cond. K_{20}, $\mu S/cm$	578.0	651.6	402.6	331.6	425.1	382.7	371.3	447.1	439.4
pH	8.14	7.56	8.02	7.97	8.21	8.34	7.85	8.11	7.81
Redox Pot., mV	55.1	74.0	186.9	208.3	81.1	86.4	117.1	92.4	118.3
COD, mg/l	14.2	13.3	15.6	2.4	19.1	14.6	22.4	39.9	40.9
MBAS, mg/l	0.27	0.59	0.34	0.04	0.17	0.10	0.10	0.11	0.16
N-NH_4, m.equiv/l	0.129	0.057	0.047	0.006	0.023	0.008	0.067	0.101	0.059
N-NO_3, m.equiv/l	0.38	0.45	0.11	0.11	0.10	0.10	0.02	0.16	0.17
N-NO_2, m.equiv/l	0.0053	0.0044	0.0046	0.0032	0.0048	0.0021	0.0026	0.0081	0.0042
Ca, m.equiv/l	4.18	4.14	3.27	2.95	3.14	3.14	2.60	3.41	3.80
Mg, m.equiv/l	1.01	1.34	0.73	0.68	0.83	1.34	0.71	1.00	0.83
Alkalin., m.equiv/l	4.41	4.79	3.38	2.93	3.29	3.17	2.96	3.66	4.01
Cl, m.equiv/l	1.35	1.60	0.77	0.55	0.98	0.85	1.19	1.01	1.03
SO_4, m.equiv/l	1.34	1.47	0.68	0.67	1.00	0.98	1.04	0.98	0.95
Pb, $\mu g/l$			58.0	97.4	30.6	25.9	32.1	19.7	9.3
Cd, $\mu g/l$			11.2	1.68	2.25	5.06	1.12	1.12	0.56
Zn, $\mu g/l$			17.2	22.8	26.1	48.8	23.1	60.0	27.4
Cu, $\mu g/l$			7.95	5.09	6.36	8.90	8.27	5.09	7.31

Table 3 Comparison between previous and present determination of some indicators of pollution in the R. Arno.

	Station							
	2		4		6		7	
	1971	*1989*	*71*	*89*	*71*	*89*	*71*	*89*
MBAS, mg/l	0.2	0.10	0.4	0.15	1.3	0.16	3.7	0.74
N-NH_4, mg/l	0.4	0.57	0.5	0.52	8	0.71	23	1.92
COD, mg/l		19.5		18.5		19.6		23.8
BOD_5, mg/l	4		5		7		30	

stream so that the Arno at station 7 is not yet affected. It should be pointed out that the presence of surfactants in surface waters is now generally less of concern than in the seventies, because of the replacement of "hard" detergents with imposed biodegradable products.

The natural variability of the water quality has to be taken into account for a river that, like almost all Italian rivers, has a variable regime with dry periods alternating with periods of full spate. This temporal pattern is evident from the data of Table 2 showing for samples of 1st May 1989, following 36.8 mm of rain in the Florentine area in the previous 24 hours, measurements are strongly affected by the river being in full spate with the concentration of the different components in the samples at a minimum. On the other hand, at other periods, specifically in January and February of that year, when the Arno was at an exceptionally low level for the winter, the surfactants are present in maximal concentrations, since the absence of dilution during a dry period is coupled with the lack of biodegradation during the low temperature of the winter months.

An interesting point arises from the samples of 4th October 1989, taken when the public authorities identified conspicuous concentrations of ammonia nitrogen in the Arno in the drinking-water plants upstream from Florence. The phenomenon was attributable to the discharge of sedimented material into a large artificial reservoir (Levane) about 50 km upstream from Florence. It was later discovered that the sediment was subject to anaerobic fermentation and thus the presence of ammonia in the river was not surprising. The observations for that day (Table 4) clearly indicate the abnormal levels of ammonia nitrogen already upstream of the town; however it may be noted that these values, even though they generated public alarm about the safety of the water supply, are of the same order or lower than those normally found downstream of the town.

On the whole, the results show that the basic composition of the water, apart from specific variables that indicate pollution, does not undergo great variations as it flows through the city of Florence. The water constantly has a slight "furring" capacity, according to an aggressivity index (AI) (Millette *et al.*, 1980)

$$AI = pH + \log[Ca] + \log[Alk]$$

of about 12 ([Ca] and [Alk] as mg/l of $CaCO_3$).

Some consideration has been given to the presence of the most common heavy metals, i.e. lead, zinc, cadmium and copper, determined as the soluble fraction after filtration through a 0.45 μm membrane. The results showed a notable variation both at the different times and at the different stations of the study. The

Table 4 Ammonia-nitrogen (mg N/l) determined October, 4th, 1989 at the various stations; comparison with average values.

Station	*Ammonia-nitrogen, mg N/l*	
	Oct. 4, 1989	*Average 1989*
1 (*)	1.96 (**)	0.49
2	1.68	0.57
3	1.36	0.60
4	1.04	0.52
5	0.56	0.60
6	0.60	0.71
7	2.66	1.92

(*) In proximity of the municipal drinking water plant, supplied from the R. Arno.

(**) Italian regulation (DPR 515/1982) allows a maximum guide value of 2 mg/l as NH_4^+ (i.e. 1.56 mg/l as N) for surface waters suitable for drinking water supply.

average values are some tens of micrograms per litre for lead and zinc, and a few micrograms per litre for cadmium and copper. The investigation, however, showed a clear distinction between metals of anthropogenic origin (lead and cadmium) and metals also present in nature, like copper and zinc. The former are very often found below sewage discharge points and their concentration thus increases as the river proceeds downstream. On the other hand, zinc and copper are found even at the last station, at concentrations that do not differ much from the means of the previous stations upstream.

An interesting observation may be made concerning the samples of 1st May 1989, with particular reference to lead. Samples taken at full spate on that day pointed to a general dilution of all the components, including heavy metals. However, lead had a value higher than any other trace metal components, possibly attributable to the abnormally high concentration at the last sampling station, located in an area of sewage collection. So the metal originating from car exhausts is deposited on the road surfaces and was washed first into the drains and then via sewage discharge into the river Arno.

A factor, not always given due consideration, is the "complexing capacity", usually defined by the amount of Cu^{2+} ion complexed by organic ligands that are present in water and wastewater (Chau and Lum-Shue-Chan, 1974; Cellini Legittimo and Pantani, 1986). The results for the samples taken along the whole river in Autumn 1988 are shown in Figure 2. The presence of ligands in the river waters seems to be evident throughout, with the exception of the first sampling station at the source of the river. This factor also includes complexing agents of natural origin, and does not always show maximum values that closely correspond to the maxima of pollution-indicating variables such as COD. A tendency to higher values is, however, seen as the river proceeds downstream. The samples taken in the Florentine reaches in spring 1989 showed a lower complexing capacity than that measured during the previous study (approx. 100 nanomol/l of Cu^{2+}) and a higher degree of dissociation of the copper complexes. A plausible explanation may be that the 1988 samples were taken in a period characterized by an intense biological activity, biodegradation replacing the larger molecules to simpler ones that better match the reaction schemes usually employed in the determination of complexing capacity.

CONCLUSIONS

The results reported undoubtedly point to a high level of water pollution in R. Arno and give an indication of the related environmental problems. To have a more comprehensive view of water quality of the surface waters throughout the Florentine area, further data are available for the Arno tributaries which flow into this river in the immediate vicinity of Florence. We feel it is not useful here to refer to all the detailed analytical findings; it is enough to give a general picture of the situation, showing in Figure 3 the mean COD values found at the various sampling stations. The same illustration shows the most important discharges of urban waste. It is easily seen that the tributaries are often in degraded state at the point of discharge of sewage. This situation is not much different from that analysed 15–20 years before and generally confirms the poor environmental

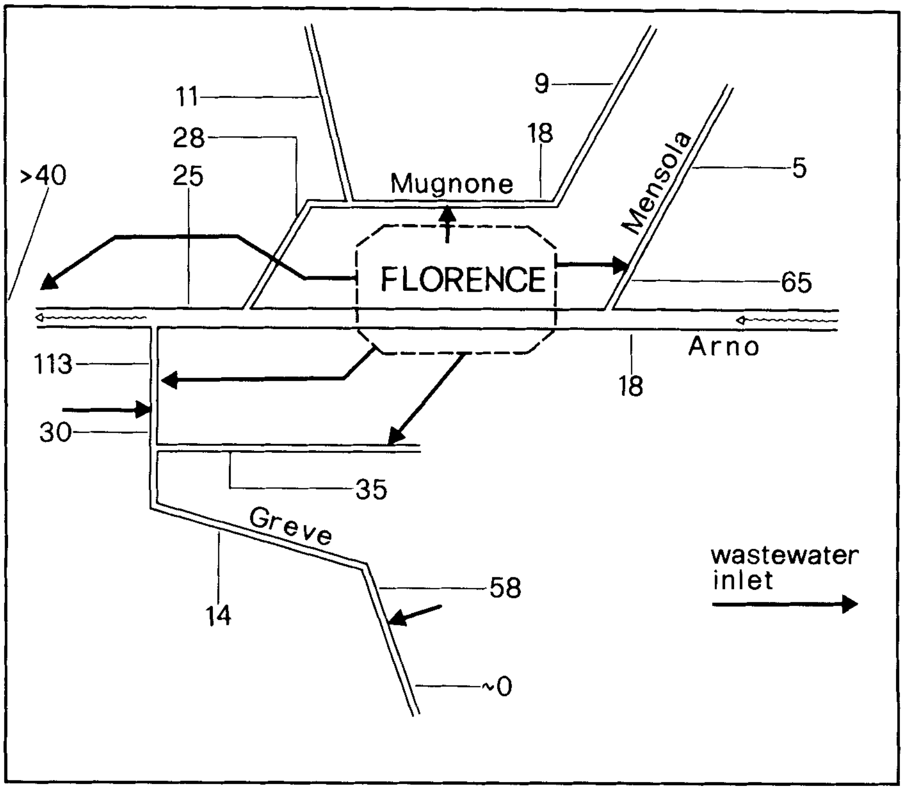

Figure 3 Mean values (mg/l O_2) of Chemical Oxygen Demand (COD) determined in R. Arno and its tributaries in the area of Florence during the year 1989.

quality due to the continuing lack, even today, of any effective treatment for the purification of urban waste.

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