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WATER QUALITY IN THE ST. LAWRENCE RIVER AT WOLFE ISLAND (Report No. EHD 97-01/I)

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Ecosystem Health Division
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Canada

Water Quality In The St. Lawrence River
At Wolfe Island (Report No. EHD 97-01/I)

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Environmental Conservation Branch
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EHD
Environment Canada

Ecosystem Health Division Report # 97-01/I

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Introduction

In 1976, Environment Canada established a monitoring station on the St. Lawrence River at Wolfe Island, near Kingston, Ontario as part of it's commitment to the Canada United States Great Lakes Water Quality Agreement (GLWQA) (Fig. 1). The monitoring program is intended to aid in the evaluation of the effectiveness of pollution control programs carried out in the Great Lakes Basin which have resulted in improvements in water quality. Specifically, data generated from this sampling station are used to identify exceedences of water quality guidelines, to assess current water quality conditions, and to evaluate trends. This report assesses water quality conditions and guideline exceedences for inorganic variables including physical parameters, major ions, nutrients and trace metals. It provides an up to date assessment for some of the variables reported on by Sylvestre et al.(1987). Trace organic contaminants data collected at the Wolfe Island station have been summarized previously for the 1989 to 1993 period (Biberhofer, 1995).

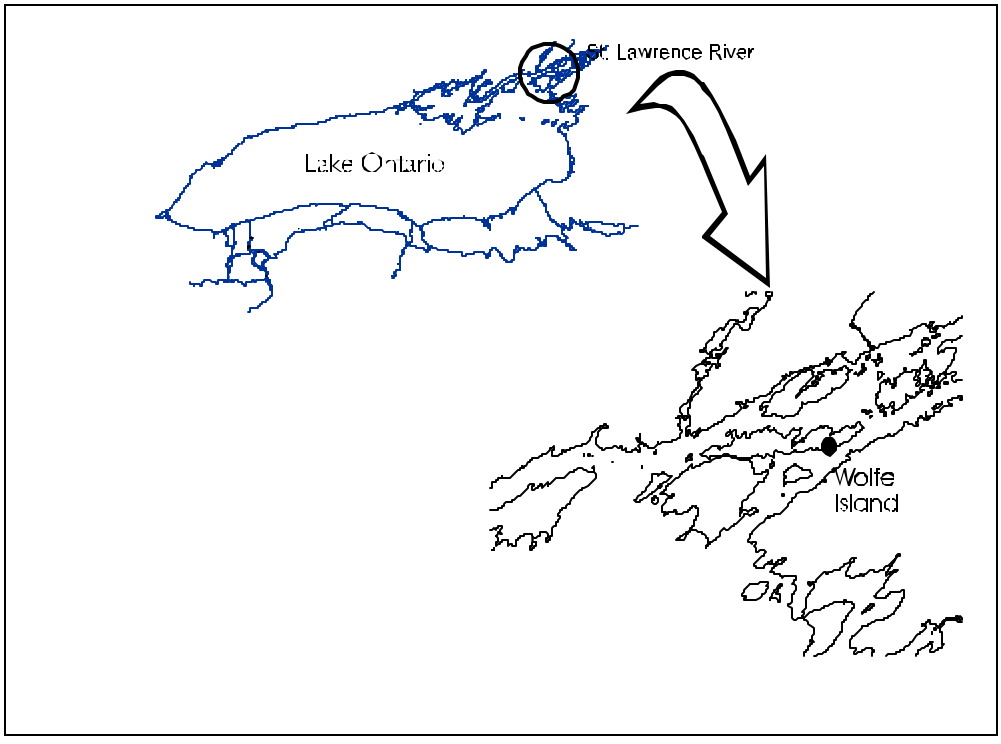

Figure 1. Wolfe Island Sampling Location.

Methods

Sampling Methods

The Wolfe Island sampling site is located along the south shore of Wolfe Island at Banford Point. Approximately 60% of the St. Lawrence River flow is in the south channel, while the north channel accounts for the remaining 40% (Casey and Salbach, 1974). The water intake is located 120m from shore and is positioned at approximately mid-depth in the water column at 11m. Water delivery to the on-shore field laboratory is by a submersible pump. A programmable timer located in the trailor/field laboratory, flushes out the intake line daily and also controls an automated sampler which collects water samples on a weekly frequency for major ions, nutrients and trace metals (Fig. 2). The sampler is housed in a refrigerator to keep all samples at 4°C until transported back to CCIW for analysis. A more detailed description of the sampling site describing the water delivery system and sampling methodology may be found in "Wolfe Island Sampling Protocol" (Kuntz, 1996). Once a month, staff visit the site to collect filtered nutrient and organic samples.

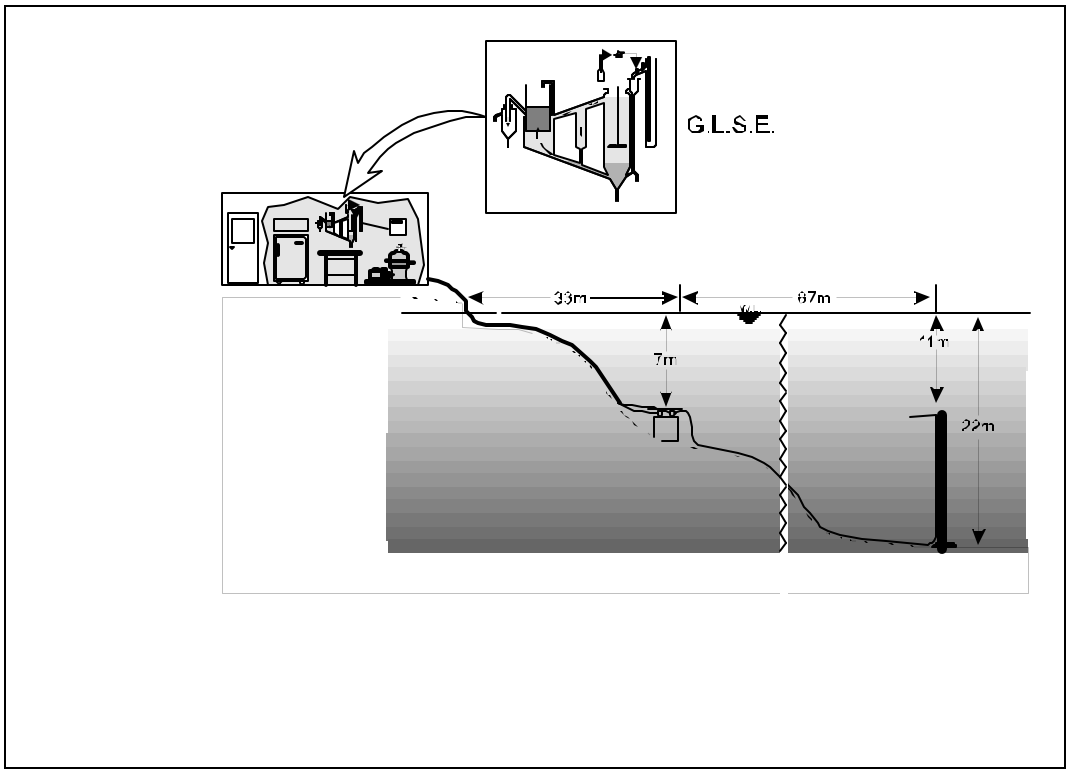

Figure 2. Wolfe Island Water Delivery System.

Analytical Methods

Weekly samples collected for major ions, nutrients and trace metals are analyzed in Burlington according to prescribed analytical methods (Environment Canada 1994a, 1994b).

Results and Discussion

Physical Parameters

Flow

Flow data is collected at the Moses-Saunders control structure located in Cornwall. In order to estimate flow at the Wolfe Island site, a nine day time of travel factor between Wolfe Island and Cornwall is incorporated. Between 1977 and 1995, annual median flow rates have varied from a low of 6850 m^3/s in 1995 to a high of 9200 m^3/s in 1986 (Fig. 3). Within year variability is indicated by the 10^{th} and 90^{th} percentile bars in the figure.

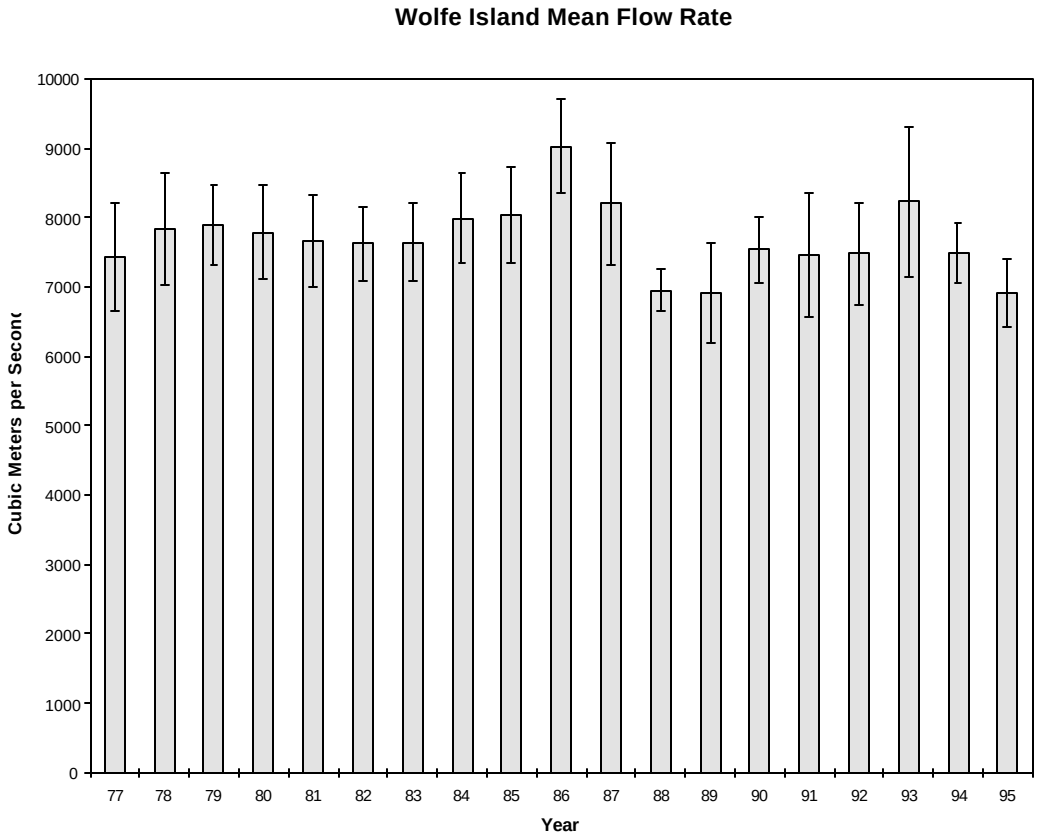

Figure 3. Wolfe Island Flow.

Specific Conductance

Conductivity has shown a decrease over the period of record, mainly due to decreases in concentrations of major ionic constituents such as chloride, sodium and calcium. Median specific conductance of 333 usie/cm was recorded in 1977. Conductivity indicated a general decreasing trend to 1996 of over 10.5%, when a median conductance of 298 usie/cm was recorded.

pH

Measurements of pH have remained quite steady over the years, with annual geometric means ranging from 7.76 to 8.11. This accounts for a range over the 1977 to 1995 time period of less than half a pH unit. These values fall within the range of 6.5 to 9.0 as outlined in Annex 1 of the GLWQA.

Turbidity

Turbidity has remained relatively constant with annual median values between 1981 and 1996 falling below 1 JTU. In more recent years, there did appear to be an increase for 1995, with the median being about 50% greater than the previous year (1994) and about 50% greater than the following year (1996). This may be the result of resuspension of solids due to storm events. There was also a noticeable increase in 1995 for other particulate dependent variables such as total phosphorus, particulate nitrogen (PN), particulate organic carbon (POC), and trace metals such as aluminum, iron, manganese and zinc.

Major Ions

Major ionic constituents are found to be distributed in the following proportions:

Cations: Ca>Na>Mg>K
Anions: HCO_3>SO_4>Cl

Chloride, sodium, and calcium annual mean concentrations indicate that there have been decreases over the period of record, while total alkalinity, sulphate and potassium data show no discernible trends. Chloride concentrations in 1976 averaged 27.7 mg/L and decreased to 20.9 mg/L in 1995, almost a 25% decrease in concentration, while calcium and sodium decreased 11.5% over the same period (Fig. 4). Decreasing trends have also been reported by L'Italien (1997) for Lake Ontario.

The major anthropogenic sources for chloride , which exhibited the largest decrease, include industrial sources, municipal wastewaters and road salting practices. Industrial inputs are considered to be the most significant source of chloride loadings to the Great Lakes (Sonzogni et al., 1983) and decreases in concentrations are primarily attributed to decreased chloride loadings from industrial sources (Whyte et al.,1990). Flow in the St. Lawrence River does not significantly affect major ion concentrations as variations in flow rates are minimal due to the Moses-Saunders control structure in Cornwall.

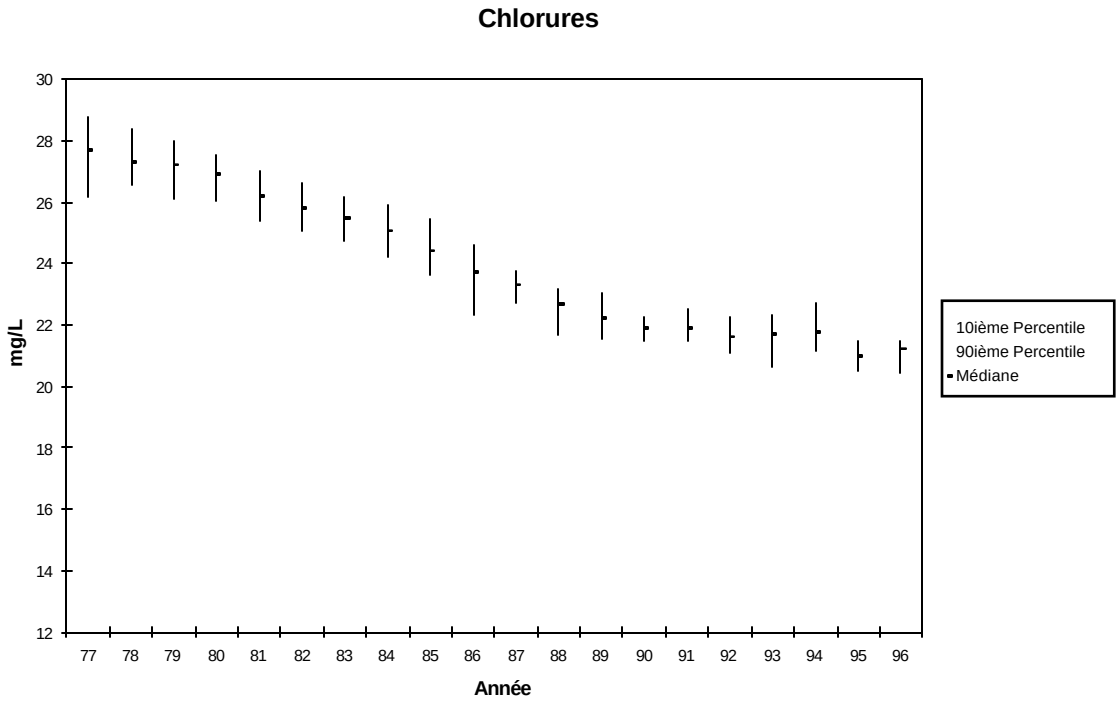

Figure 4. Chloride Concentrations at Wolfe Island.

Magnesium concentrations declined slightly over the 1977 to 1986 time period and then indicate a slight increasing trend from 1986 to 1996. This increase corresponds to decreases in chlorophyll *a* in Lake Ontario and decreases in suspended particulate matter (SPM) at the Wolfe Island sampling station. Magnesium is required by chlorophyllous plants as the magnesium porphyrin of the chlorophyll molecule. It is also important as a micronutrient for algae (Wetzel, 1975). As there is less uptake of magnesium from the water column, concentrations appear to be increasing slightly (Fig. 5). Similar trends have been observed in magnesium and chlorophyll *a* in the Niagara River and Lake Erie (per. communication, D.J. Williams).

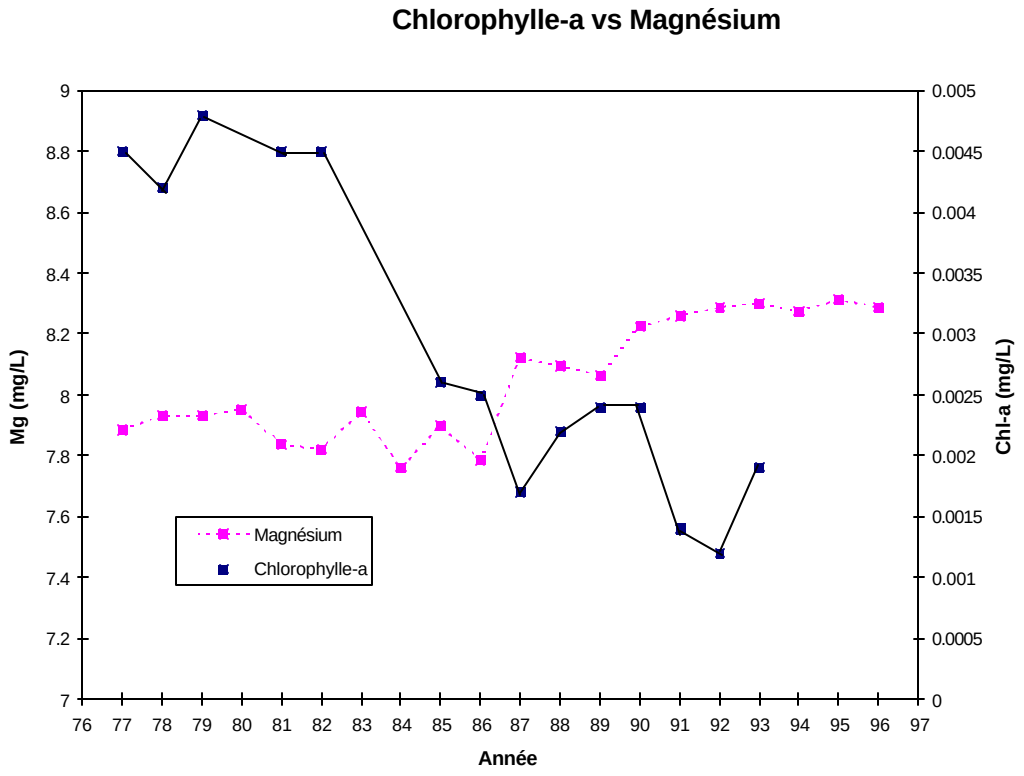

Figure 5. Chlorophyll *a* vs Magnesium at Wolfe Island.

Nutrients

Total phosphorus has decreased over the period of record from 0.016 mg/L in 1977 to a low of 0.008 mg/L in 1996. Similar decreasing trends for Lake Ontario have been reported (L'Italien, 1997). Results from 1995 are somewhat anomalous in that there was a sharp increase in the annual median concentration, for no apparent reason. This was also the case found at the Niagara River monitoring stations (pers. Communication, K.W. Kuntz). Data collected in 1996 show concentrations more in line with the 1994 results and other previous years. Reductions can be attributed in part to phosphorus removal at sewage treatment plants in the Great Lakes Basin and to decreases in phosphorus used in fertilizer, which has been steadily decreasing from the late 1970's (Fig. 6).

Nitrate increased in concentration from 1977 through 1986, then decreased until the early 1990's when it began to increase once again. The overall trend line for the period of record is that of increasing concentrations. Data on nitrogen in fertilizer indicate increasing use to a peak in 1985 of approximately 240,000 metric tonnes per year for the province. This has since decreased to around 175,000 tonnes in 1995 (Fig. 7).

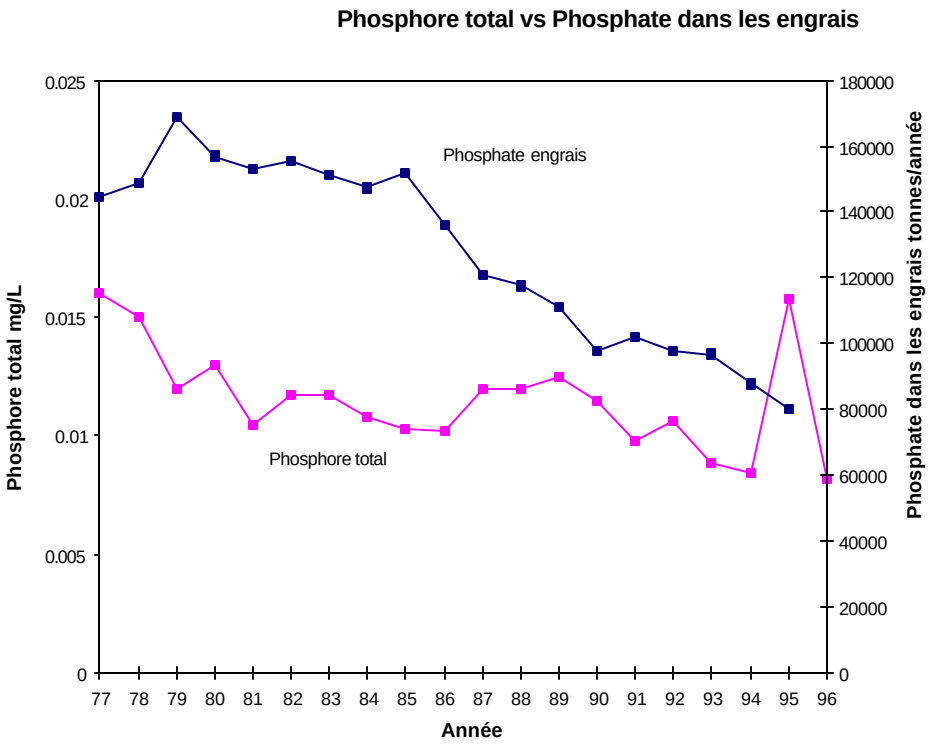

Figure 6. Total Phosphorus vs Phosphate Fertilizer.

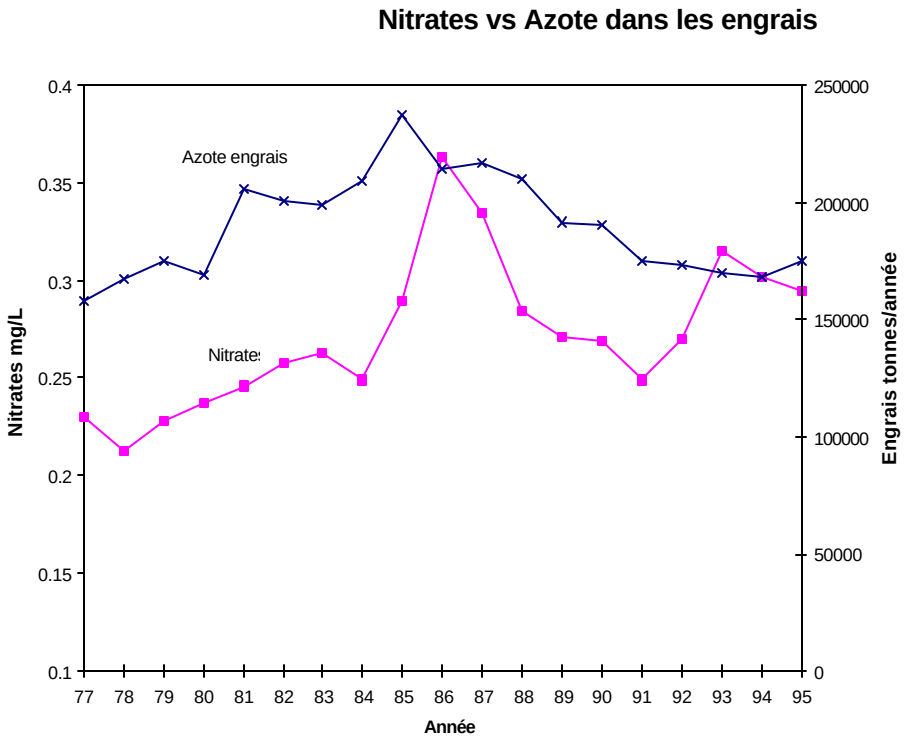

Figure 7. Nitrate vs Nitrogen Fertilizer.

Total Kjeldahl nitrogen (TKN), which is a measure of ammonia and organic nitrogen, has remained fairly constant throughout the period of record. Median concentrations have ranged from 0.180 to 0.232 mg/L. With the exception of the lowest annual median (0.180 mg/L) which was recorded in 1978, the next lowest annual median is 0.201 mg/L, which even tightens up the range more, if the 1978 median is considered an anomaly.

Silica concentrations at Wolfe Island remained relatively constant into the early 1990's but in recent years have started to show an increasing trend (Fig. 8). This may be due to less uptake by diatoms and algae, which have decreased in recent years due to the invasion of *Dreissena* and the grazing pressure exerted by these filter-feeding mussels.

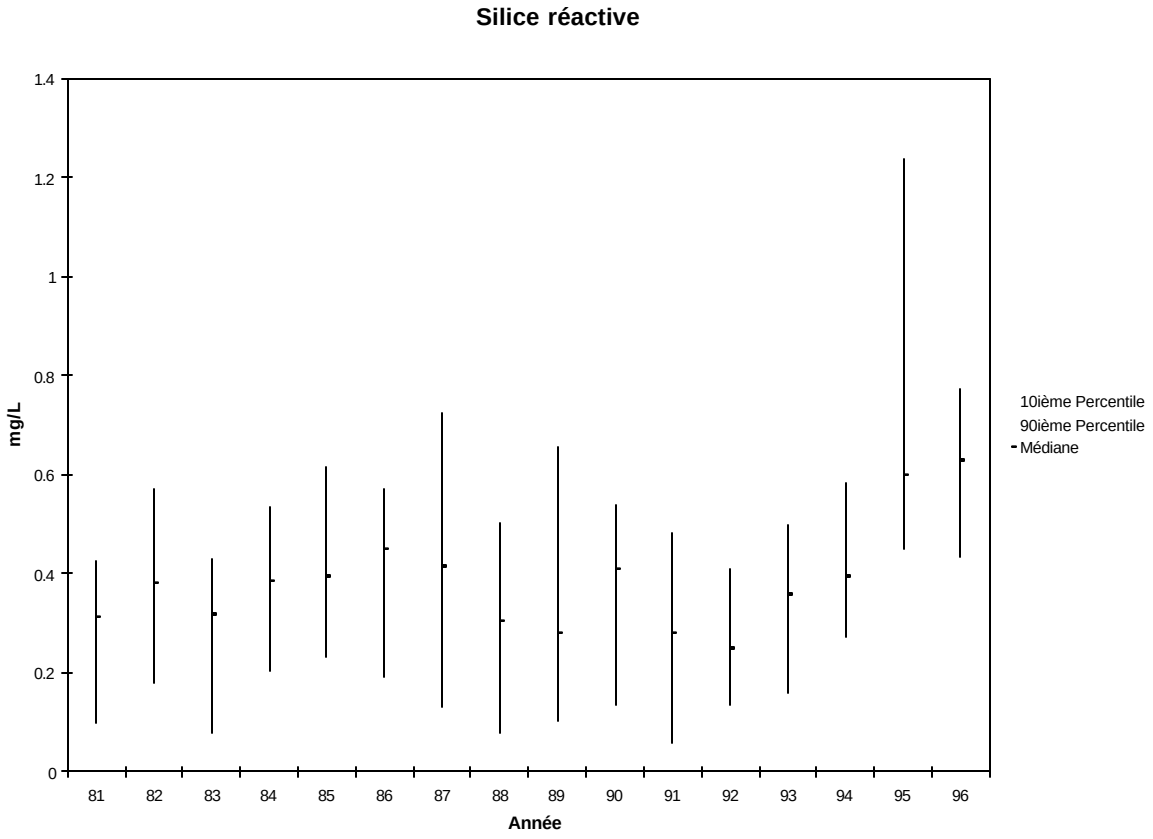

Figure 8. Reactive Silica at Wolfe Island.

Both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations were quite constant throughout the sampling period from 1989 to 1995. Mean DIC concentrations ranged from a low of 20.7 mg/L in 1991 to an annual mean of 23.2 mg/L in

1993 with no evident temporal trends. Annual means for DOC ranged from 2.42 mg/L to 2.84 mg/L and as was the case with DIC, there were no discernible temporal trends.

Suspended particulate matter, as calculated from solids concentrations obtained from monthly centrifugation over a 24 hour period at the Wolfe Island site, has declined from 1.4 mg/L in 1991 to less than 0.2 mg/L in 1995 (Fig. 9). There have also been corresponding decreases in particulate organic carbon and particulate nitrogen recorded at this station. Both POC and PN have decreased overall in the order of 50% from 1992 to
1996, although in 1995 there were increases evident. Environment Canada surveillance data from Lake Ontario shows that mean summer open lake chlorophyll *a* concentrations have declined from in excess of 0.004 mg/l in the early 1980's to less than 0.002 mg/l in 1993, the last year for which there is data available. This downward trend is also corroborated by Fisheries and Oceans who have a historical database for Lake Ontario which shows significant decreases in chlorophyll *a* over the April to October sampling period between 1987 and 1995 (DFO Bioindex Data Base, Ora Johannsson, unpubl. data).

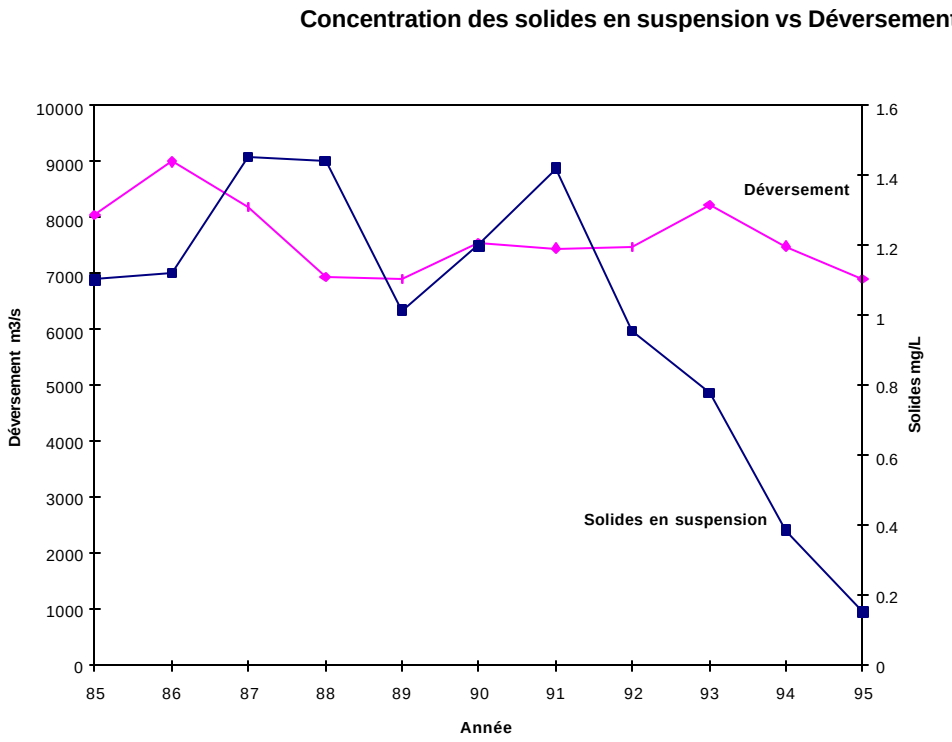

Figure 9. Suspended Solids Concentration vs Discharge

With increases in 1995 for turbidity, POC, PN, total phosphorus, and some trace metals, it would be expected to find a corresponding increase in SPM for the same year, not the decrease that is reported. This may be due to the sampling frequency which is weekly for phosphorus,

turbidity, and metals, while SPM, PN and POC are collected monthly. The discrepancy may also be due in part to the decreasing accuracy of calculating SPM concentrations as the sample size decreases.

Trace Metals

A total of 19 metals have been analyzed from samples collected at the Wolfe Island sampling station over the years. The period of record varies by parameter and sampling protocols have changed to some degree over the years as well. Improved bottle washing, sampling techniques and reductions in analytical detection limits have resulted in generally lower concentrations being detected for those variables that have been traditionally at or near the detection limit. Time plots for all 19 metals analyzed, including annual median, 10^{th} and 90^{th} percentile concentrations are presented in Appendix 1.

Table 1. Trace Metals Period of Record and Detection Frequency.

	Période	L-Marqué	Non-Marqué	% L-Marqué
Aluminium	78-96	4	584	0.68
Arsenic	88-96	0	132	0.00
Baryum	94-96	1	170	0.58
Béryllium	86-96	616	12	98.09
Cadmium	77-96	1060	86	92.50
Chrome	77-96	252	892	22.03
Cobalt	86-96	245	383	39.01
Cuivre	77-96	32	1113	2.79
Fer	77-96	0	1141	0.00
Plomb	77-96	808	337	70.57
Lithium	86-96	0	609	0.00
Manganèse	77-96	258	874	22.79
Mercure	83-96	141	32	81.50
Molybdène	86-96	0	628	0.00
Nickel	77-96	137	1009	11.95
Sélénium	88-96	13	110	10.57
Strontium	86-96	0	628	0.00
Vanadium	86-96	19	609	3.03
Zinc	77-96	206	938	18.01

Data summaries including median and 90^{th} percentile ranges over the period of record are provided for metals for which there are GLWQA objectives as set out in Annex 1 (Table 2) and also for the remaining metals for which there are no GLWQA objectives (Table 3).

Beryllium, cadmium, lead and mercury were metals with the highest frequency of results below the detection limit, ranging from 70.6% for lead to 98.1% for beryllium (Table 1). There are

currently no specific objectives for beryllium in Annex 1 of the Great Lakes Water Quality Agreement (IJC, 1989).

The GLWQA specifies an objective for cadmium of 0.0002 mg/L for the protection of aquatic life. From 1977 to 1986 the annual 90th percentile concentration was L0.001 mg/L. From 1987 to 1996, the detection limit for cadmium was 0.0001 mg/L and the annual 90th percentile concentrations over that time period did not exceed the objective of 0.0002 mg/L.

Non detectable concentrations of lead were found in slightly more than 70% of the samples. Concentrations over time reflect more the changing detection limits, than changes in the environment. Median concentrations ranged from 0.001 mg/L in the 1977-1985 time period to L0.0001 for the 1986 to 1996. In this latter time period when detection limits were lowered, the 90th percentile concentration did not exceed 0.0001 mg/L, which is well below the GLWQA objective of 0.025 mg/L.

Table 2. GLWQA OBJ. and Median and 90th Percentile Ranges

	Période	**Obj. AQEGL**	**Étendue des médianes (mg/L)**	**Étendue 90ième percentile (mg/L)**
Arsenic	88-96	0.05	0.0005 to 0.0006	0.0006 to 0.0007
Cadmium	77-96	0.0002	< Lim. Dét.	0.0001 to 0.001
Chrome	77-96	0.05	L0.001 to 0.001	0.0003 to 0.005
Cuivre	77-96	0.005	0.0009 to 0.0135	0.0011 to 0.0499
Fer	77-96	0.3	0.010 to 0.145	0.035 to 0.358
Plomb	77-96	0.025	L0.0002 to 0.002	L0.0002 to 0.003
Mercure*	83-96	0.2	L0.005 to 0.01	L0.01 to 0.0147
Nickel	77-96	0.025	0.0006 to 0.002	0.0007 to 0.007
Sélénium	88-96	0.01	0.0001 to 0.0002	0.0002 to 0.0003
Zinc	77-96	0.03	L0.001 to 0.003	0.0008 to 0.0099
* ug/L				

Mercury was below the detection limit in 81.5% of the samples analyzed. Annual median concentrations over the sampling period were all below the detection limit. Ninetieth percentile concentrations ranged from below the detection limit to 0.015 ug/L, which is well below the GLWQA objective of 0.2 ug/L. It should be noted that the objective is set for a filtered sample, while all samples collected at Wolfe Island for mercury are whole water samples.

Arsenic, chromium, copper, iron, nickel, selenium and zinc represent seven of the fifteen remaining metals that have been analyzed at Wolfe Island over the years. Frequency of non-detects for this set of metals ranges from 0% up to 22% for chromium (Table 1). There are GLWQA objectives established for these metals.

For the period of record extending from 1986 to 1996, annual median arsenic concentrations have been very stable ranging from 0.5 to 0.6 ug/L, while the annual 90th percentile concentrations ranged from 0.6 to 0.7 ug/L. These concentrations fall significantly below the objective of 50 ug/L as stated in the GLWQA.

Slightly over 22% of chromium observations were found to be below the detection limit between 1977 and 1996. Annual median concentrations ranged from below the detection limit to 0.001 mg/L. The range for the 90th percentile concentrations was from a low of 0.0003 to 0.005 mg/L. Concentrations found in the 90th percentile range were considerably below the GLWQA objective of 0.050 mg/L.

Just under 3% of samples collected for copper analysis were found to be below the detection limit. Median concentrations ranged from a low of 0.009 mg/L to a high of 0.0135 mg/L, while 90th percentile concentrations ranged from a low of 0.0011 mg/L to a high of 0.0499 mg/L. The majority of the high values were detected in the early years of the program and there were often exceedences of the GLWQA objective of 0.005 mg/L for copper. However, with improved sampling protocols, there were no exceedences of the objective found for either annual median and 90th percentile concentrations from 1985 to 1996.

All iron results for the period of record from 1977 to 1996 were above the detection limit. Median concentrations ranged from 0.010 mg/L to 0.145 mg/L. All median concentrations were below the GLWQA objective of 0.300 mg/L. There were exceedences of the guideline for the 90th percentile concentration in 1978 with an annual 90th percentile concentration of 0.552 mg/L, and also in 1982 with a 90th percentile concentration of 0.358 mg/l. As iron is one of the most common elements in the earth's crust and the frequency of exceedences is very low in recent years, there does not appear to be any concern regarding the protection of aquatic life.

Table 3. Median and 90th Percentile Ranges.

	Période	**Étendue médiane (mg/L)**	**Étendue 90ième percentile (mg/L)**
Aluminium	78-96	0.011 to 0.052	0.023 to 0.251
Baryum	94-96	0.022 to 0.023	0.023 to 0.031
Béryllium*	86-96	L0.05	L0.05 to 0.05
Cobalt	86-96	L0.0001 to 0.0002	0.0001 to 0.0010
Lithium	86-96	0.0020 to 0.0036	0.0022 to 0.0039
Manganèse	77-96	L0.006 to 0.009	0.002 to 0.0377
Molybdène	86-96	0.0010 to 0.0011	0.0011 to 0.0013
Strontium	86-96	0.168 to 0.181	0.173 to 0.185
Vanadium	86-96	0.0002 to 0.0004	0.0003 to 0.0008
* ug/L			

Twelve percent of nickel samples were below the detection limit over the sampling period. Annual median concentrations ranged from 0.0006 mg/L to 0.001 mg/L. Ninetieth percentile concentrations were in the range of 0.0007 to 0.007 mg/L which is well below the objective set at 0.025 mg/L for the protection of aquatic life.

Selenium concentrations have remained steady throughout the period of record from 1988 to 1996, with slightly more than 10% of the observations falling below the detection limit. Over this time period, the annual median concentrations ranged from 0.0001 to 0.0002 mg/L, while 90th percentile concentrations ranged from 0.0002 to 0.0003 mg/L. These values fall well below the aquatic life guideline of 0.010 mg/L as set out in the GLWQA.

Zinc has been sampled from 1977 to 1996 with a frequency of samples below the detection limit of 18%. Annual median concentrations over this time period ranged from less than the detection limit to a high of 0.003 mg/L. The 90th percentile concentration range was from a low of 0.0008 mg/L to a high of 0.0099 mg/L. All 90th percentile concentrations were well below the aquatic life objective of 0.030 mg/L.
There are no GLWQA Annex 1 aquatic life guidelines for the remaining 8 trace metals that are analyzed at the Wolfe Island station. Ranges for annual medians and 90th percentiles are summarized in Table 2 along with their period of record.

Summary

Chloride, sodium and calcium have shown a continued decreasing trend over the period of record. This is also evident for specific conductance. Similar trends reported by Sylvestre et al. (1987), for the time period from 1977 to 1983 at this site, have continued to the present but the rate of decrease is reduced.

With the exception of 1995, the annual median concentrations for total phosphorus displays an overall decreasing trend from 0.016 mg/L in 1977 to 0.008 mg/L in 1996. Nitrate on the other hand, has shown an overall steady increase.

Annual median and 90th percentile concentrations of trace metals fell below the Annex 1 objectives the majority of time, as set out in the GLWQA. Any exceedences that did occur were prior to 1986.

Acknowledgments

Special thanks are extended to Bruce Harrison for overseeing the operation of the site, his technical support, and collection of monthly samples at the station; Mrs Elizabeth Woodman for the weekly collection of samples; Mary Lou Archer for keeping everyone organized; and NLET for their timely analysis of samples.

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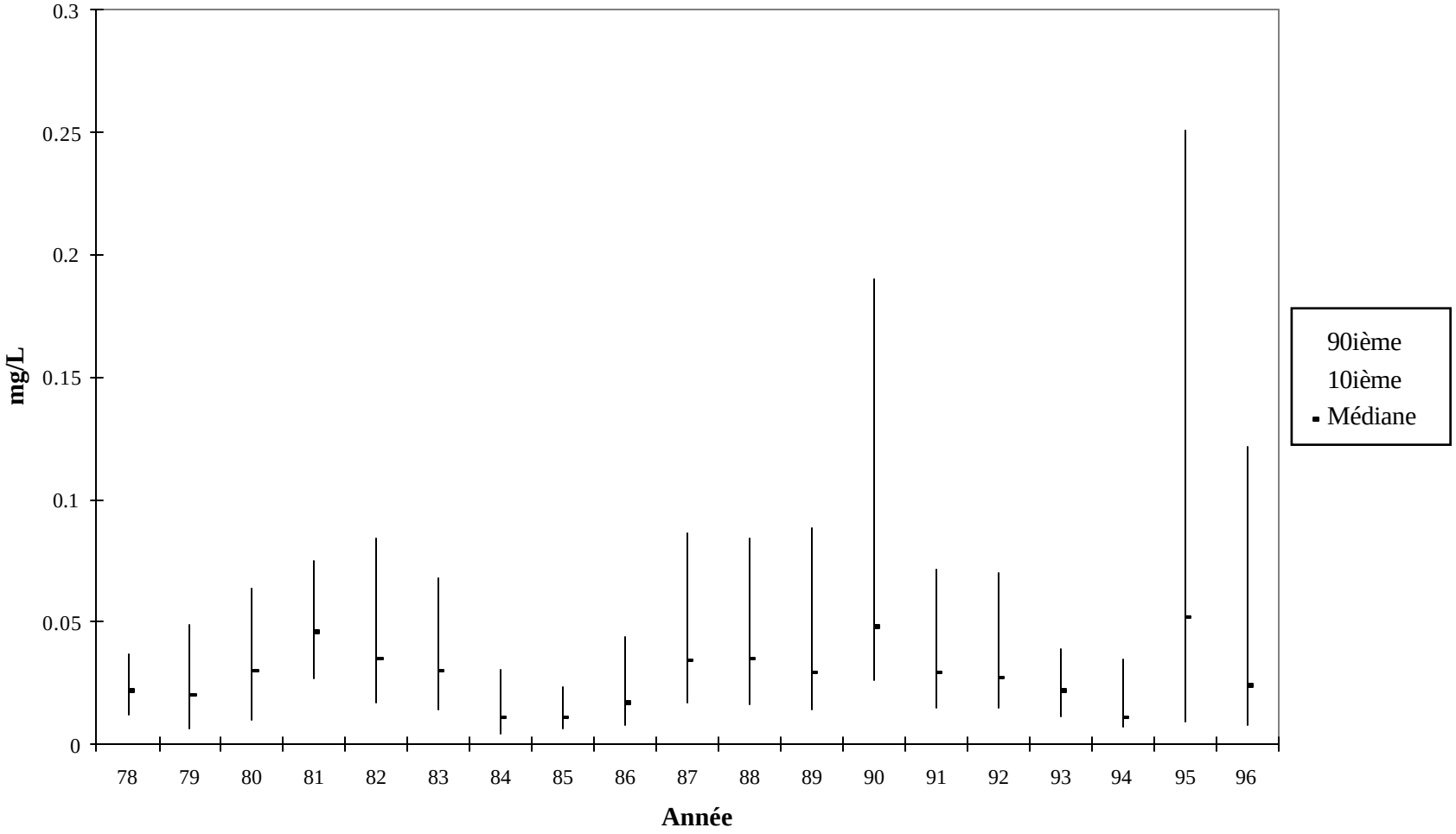
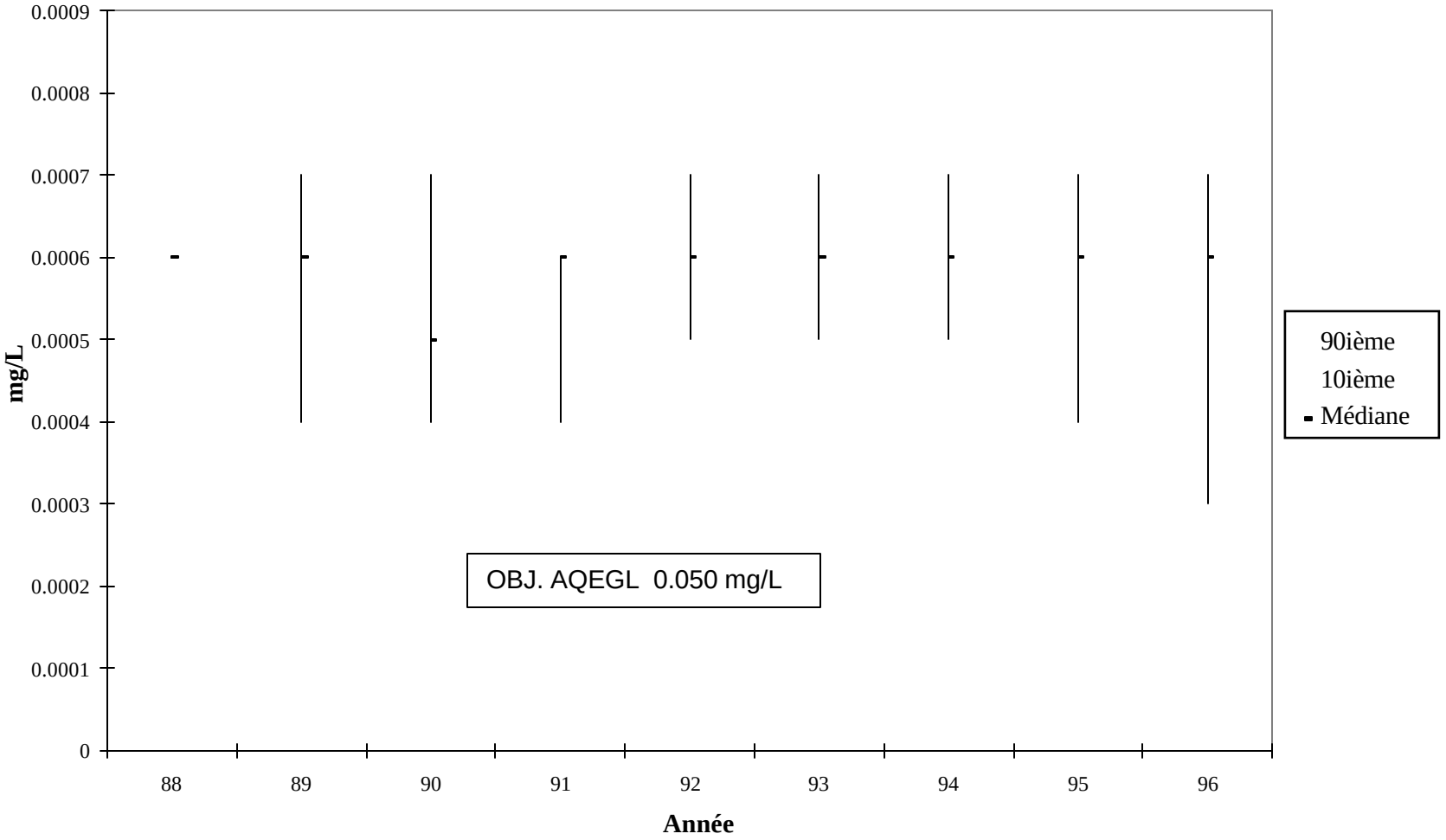
Appendix A

Aluminium total



Arsenic total



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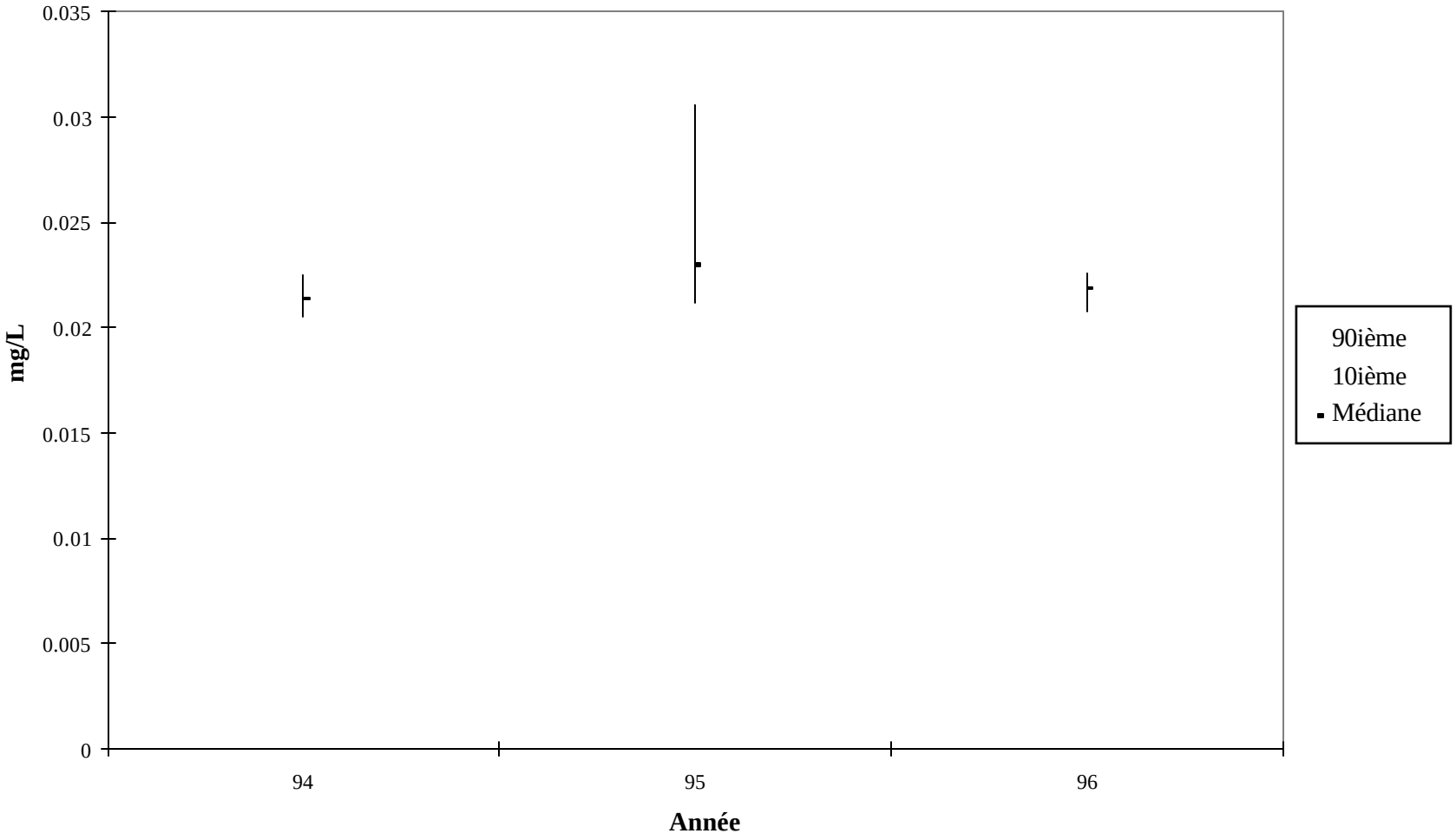

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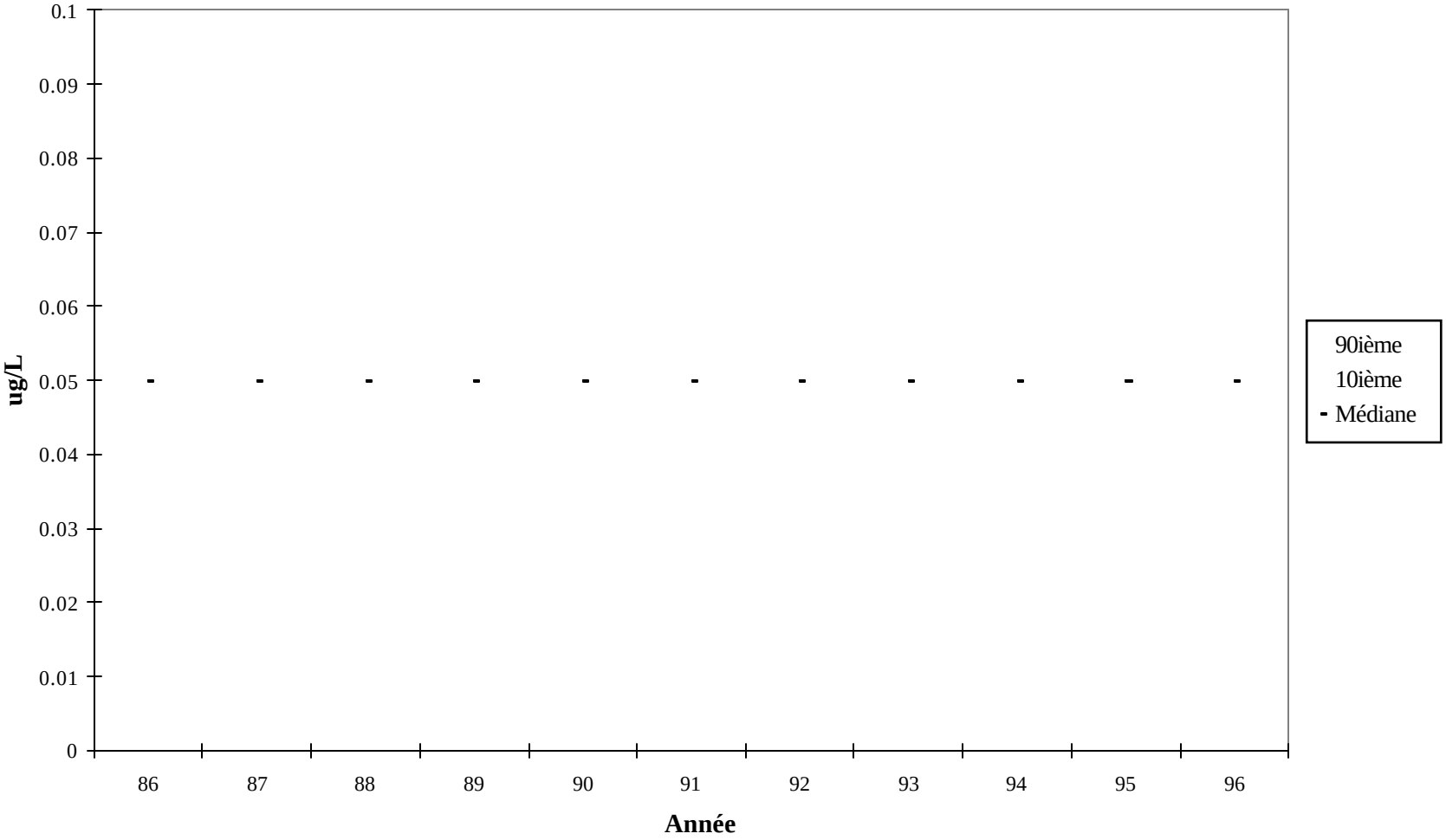

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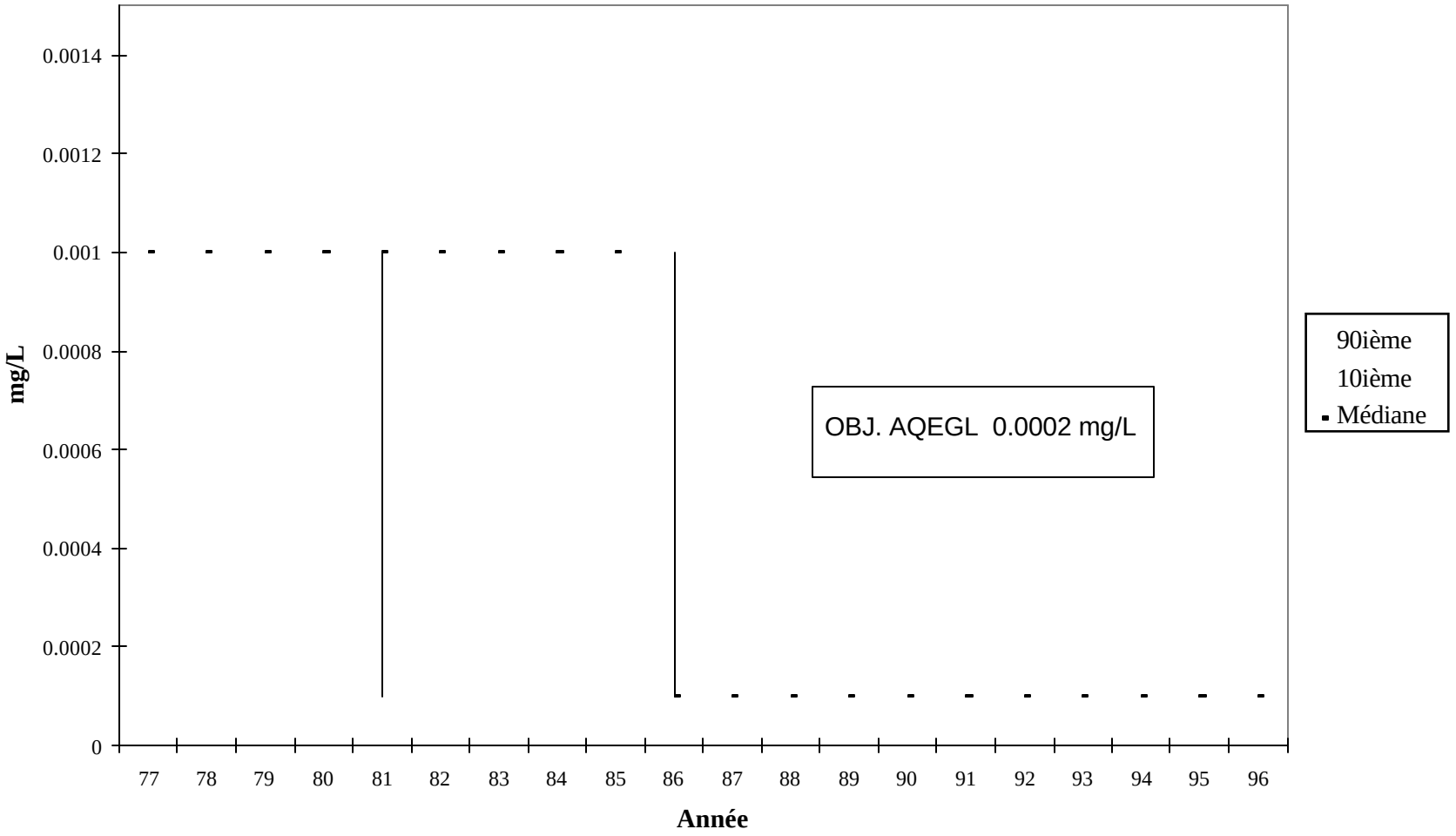

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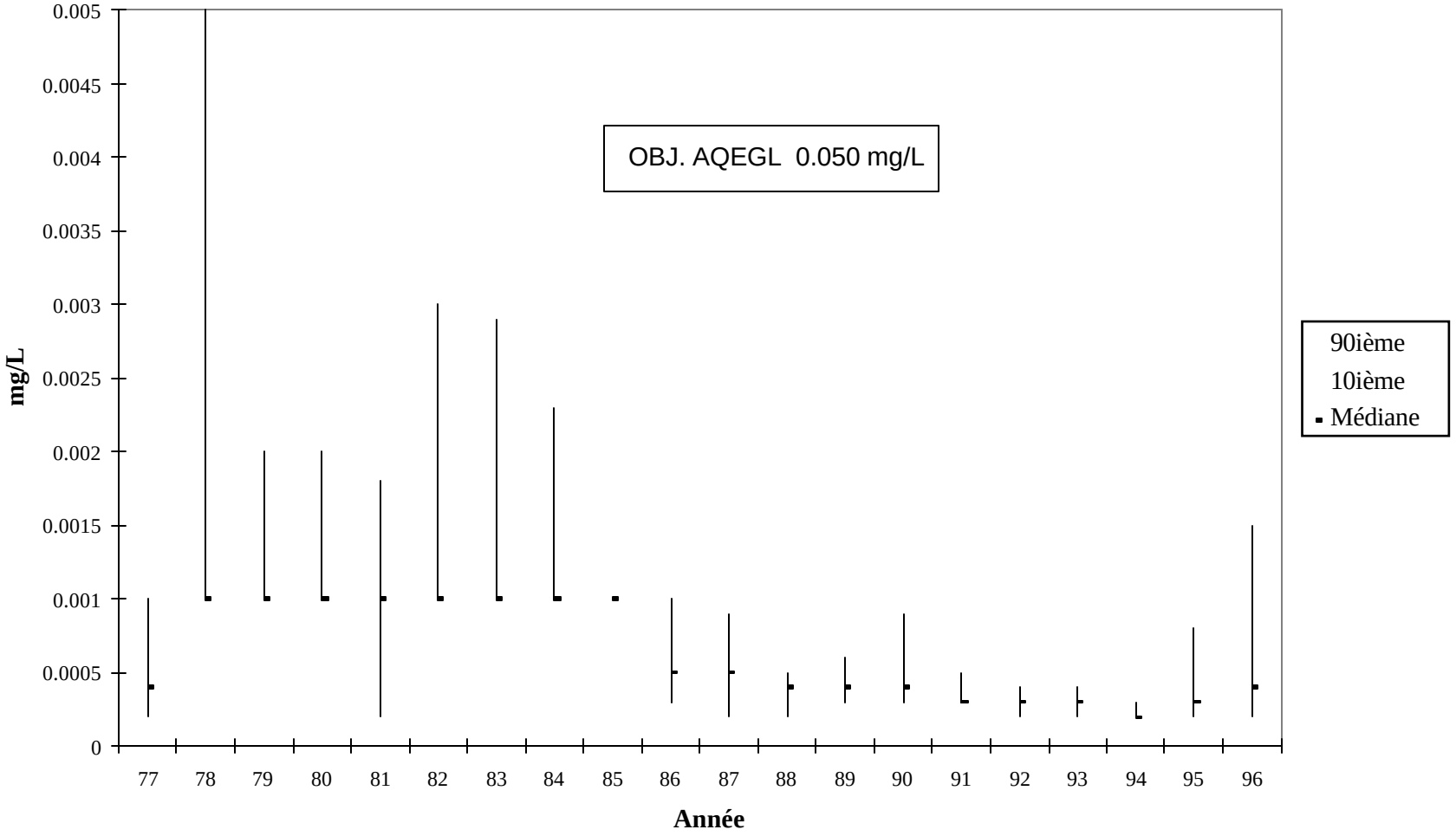

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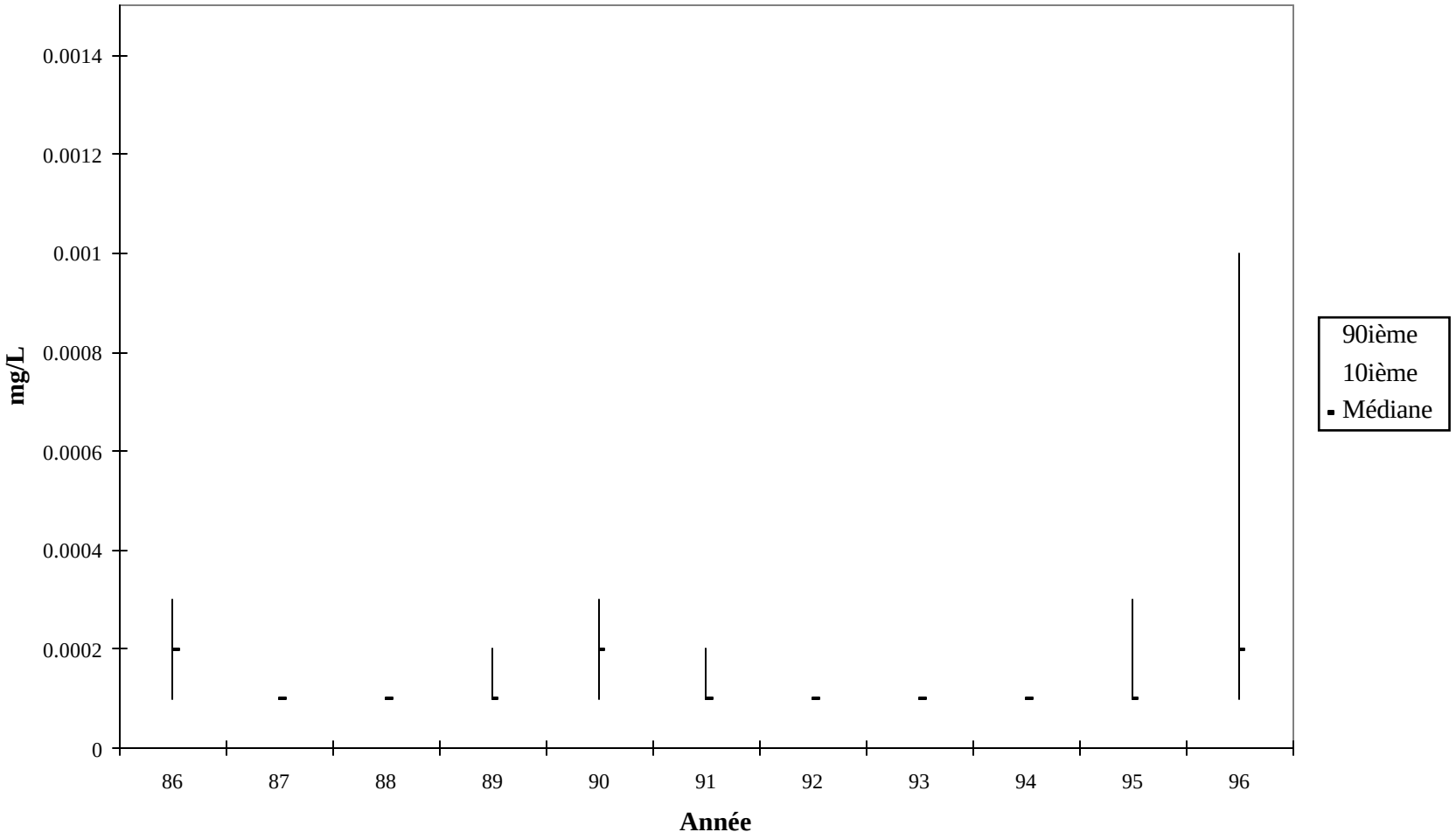

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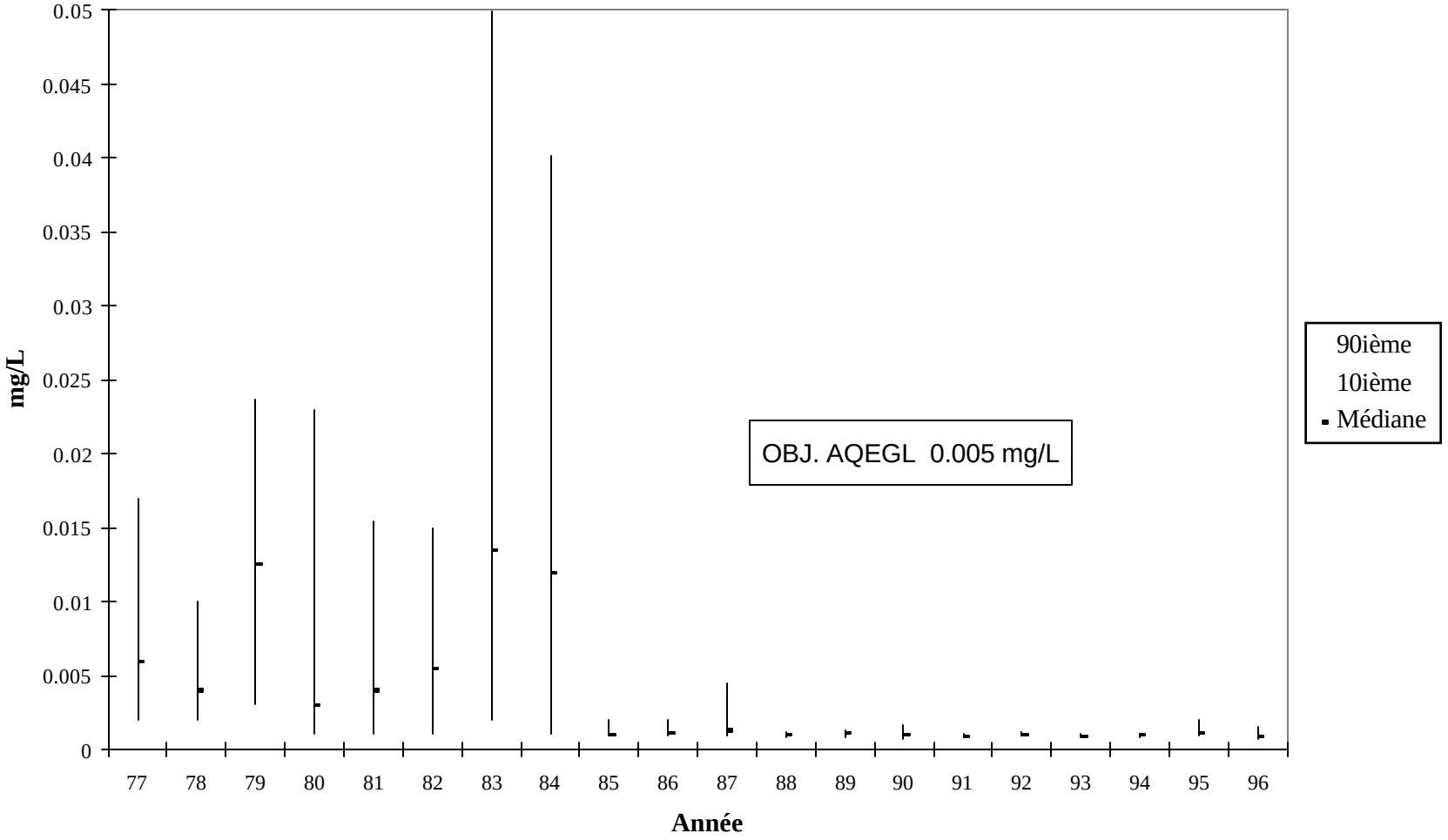

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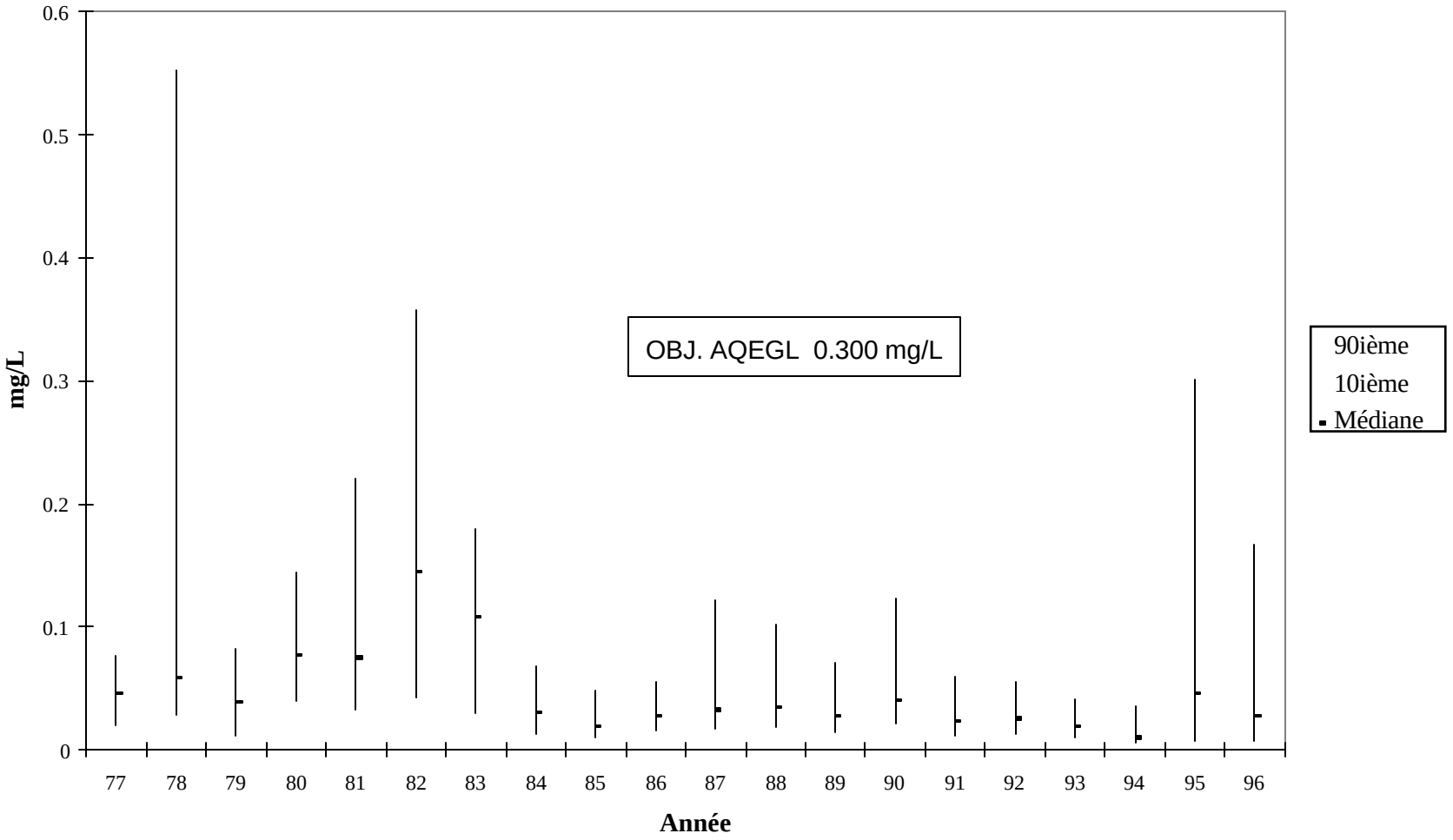
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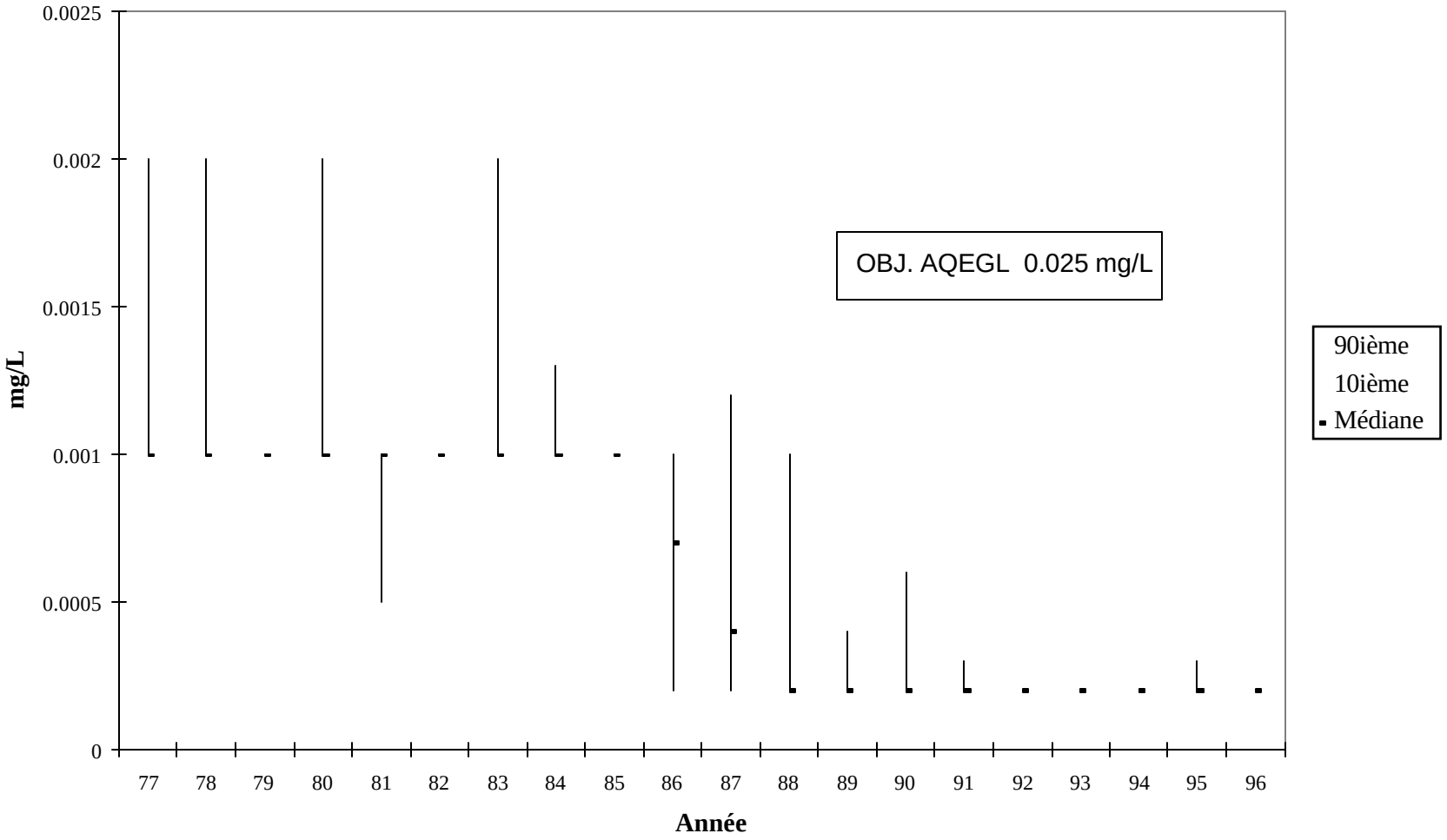
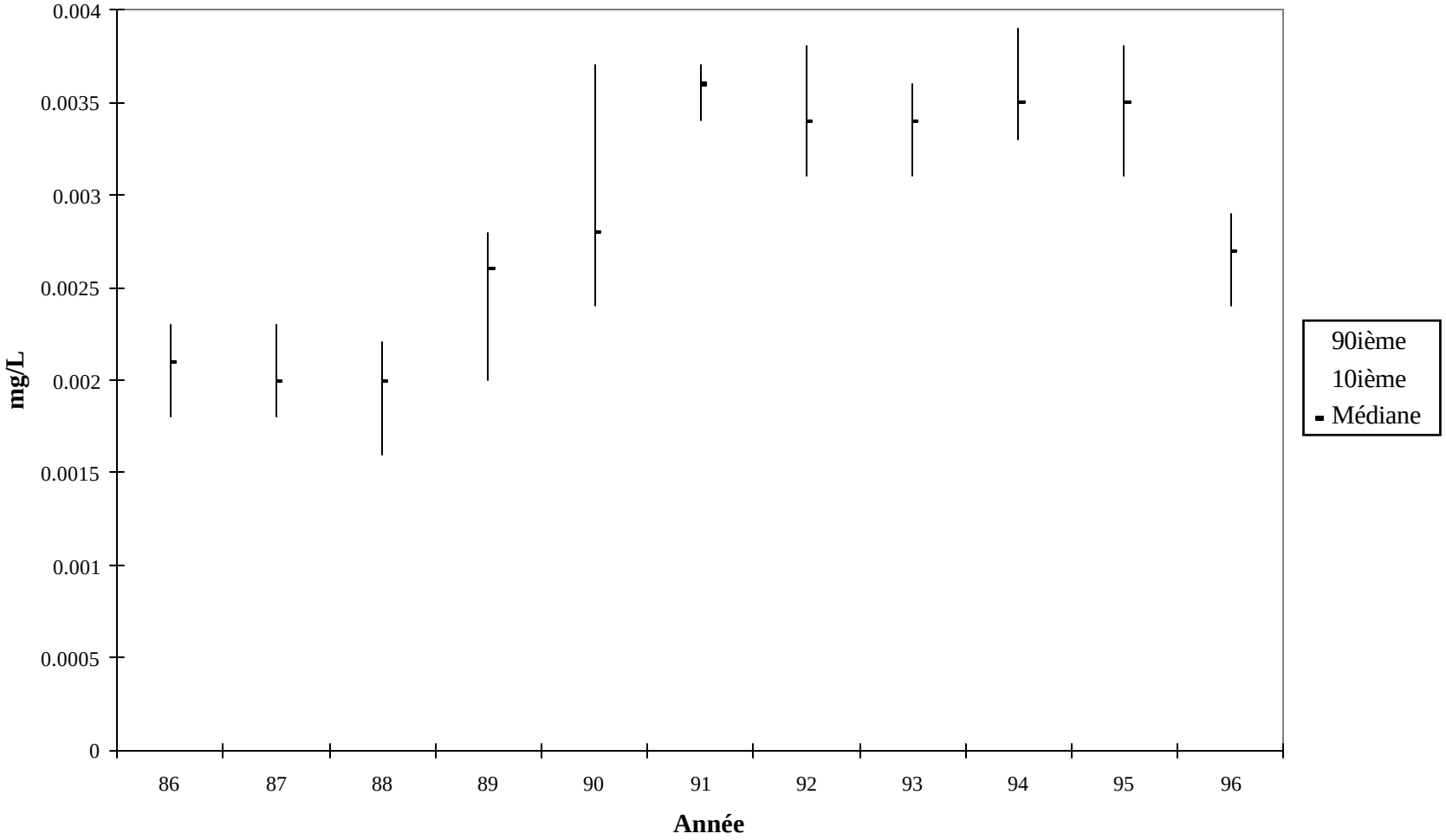
95
96
Année

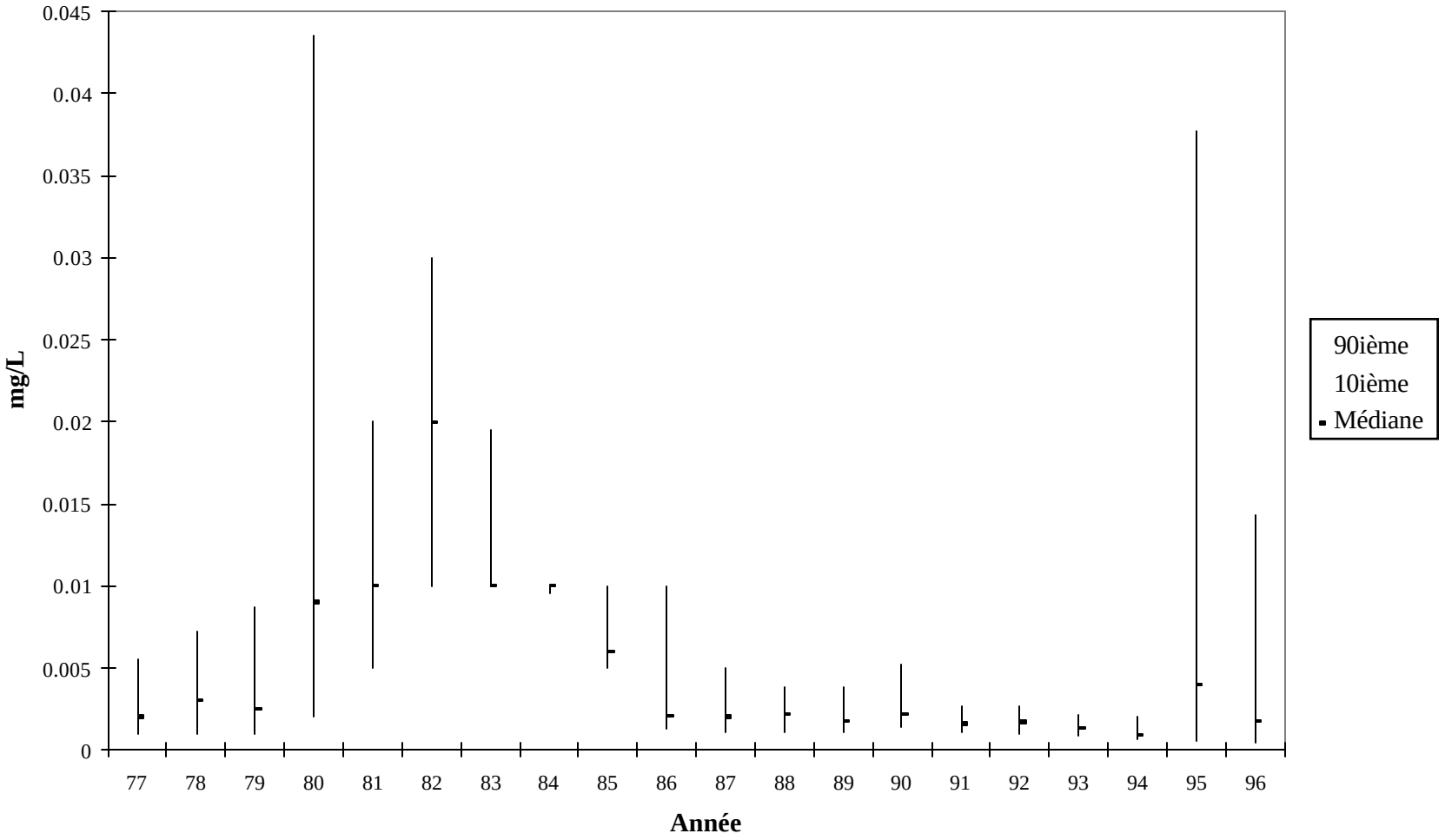
Plomb total


0.0025
0.002
0.0015
0.001
0.0005
0
mg/L
OBJ. AQEGL 0.025 mg/L
90ième
10ième
Médiane
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
Année

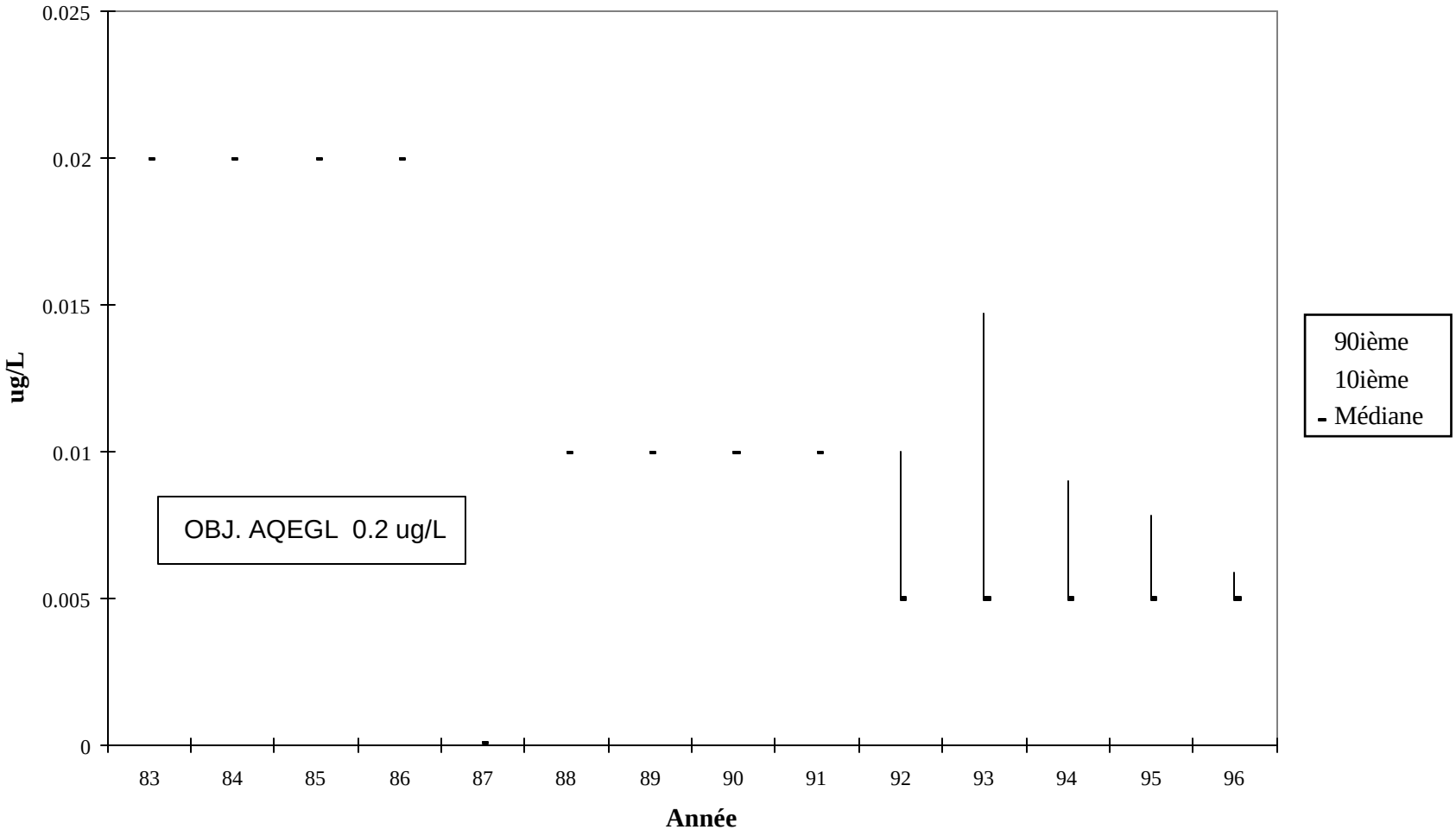
Lithium total



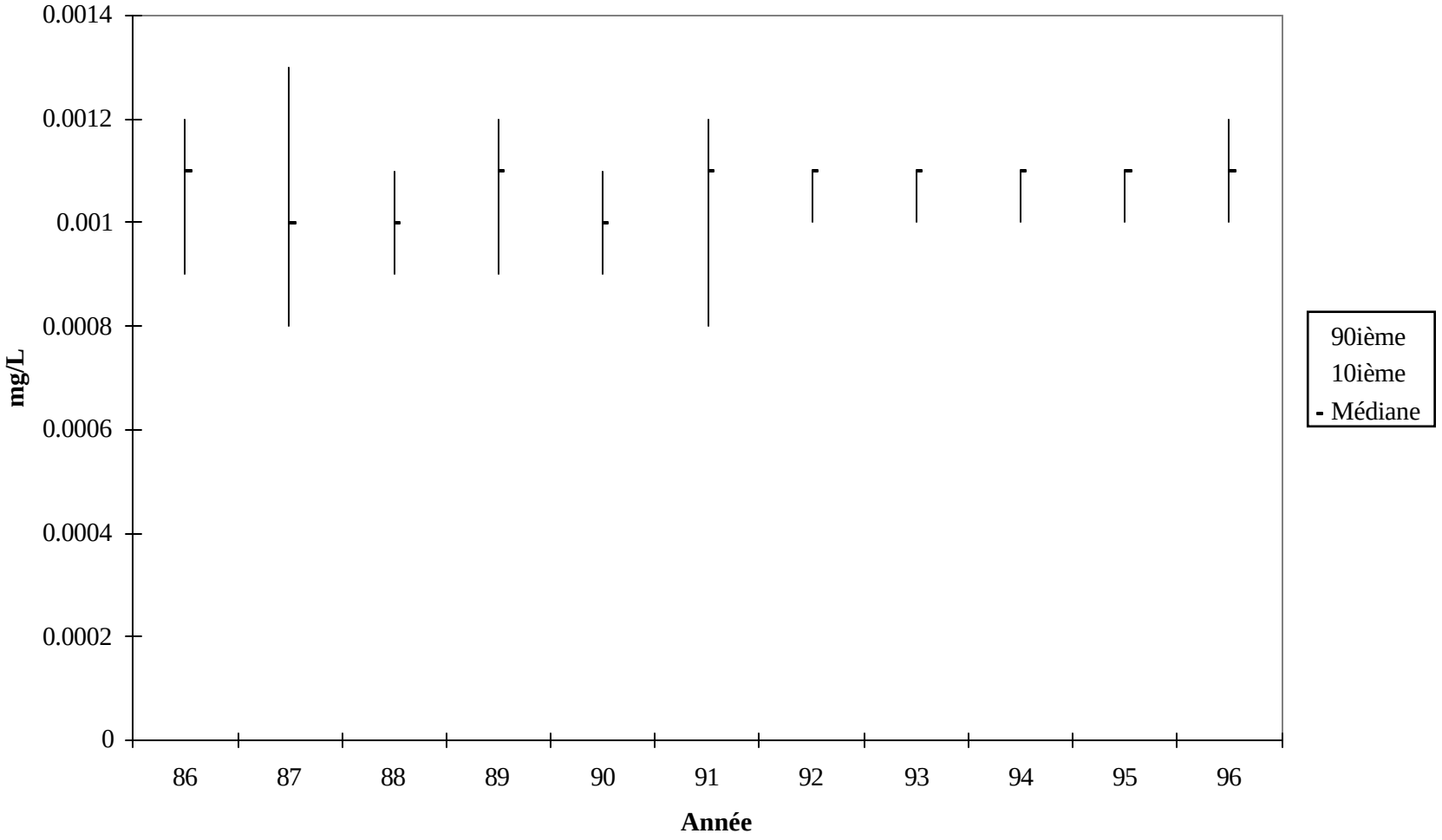
Manganèse total



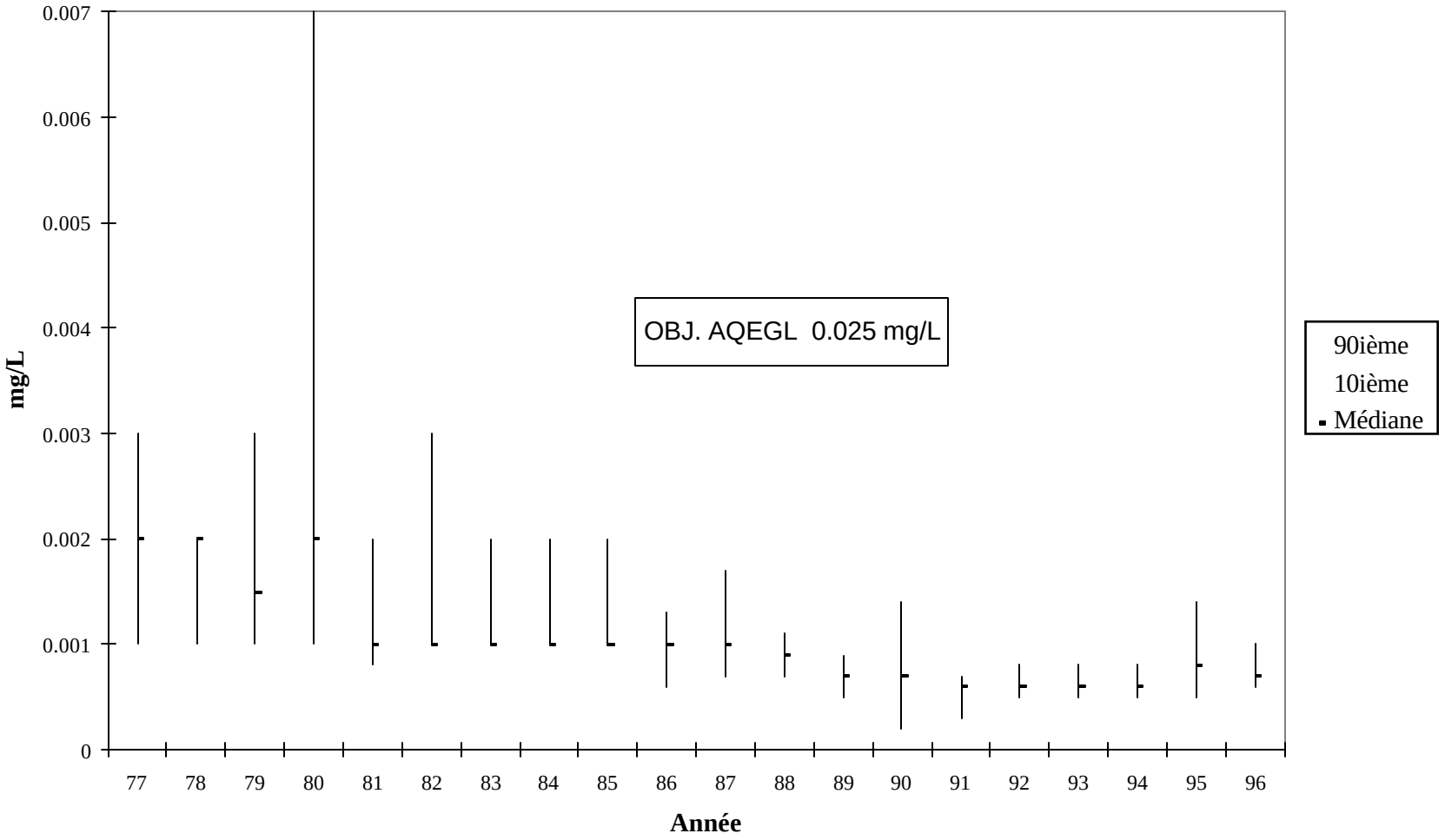
Mercure total



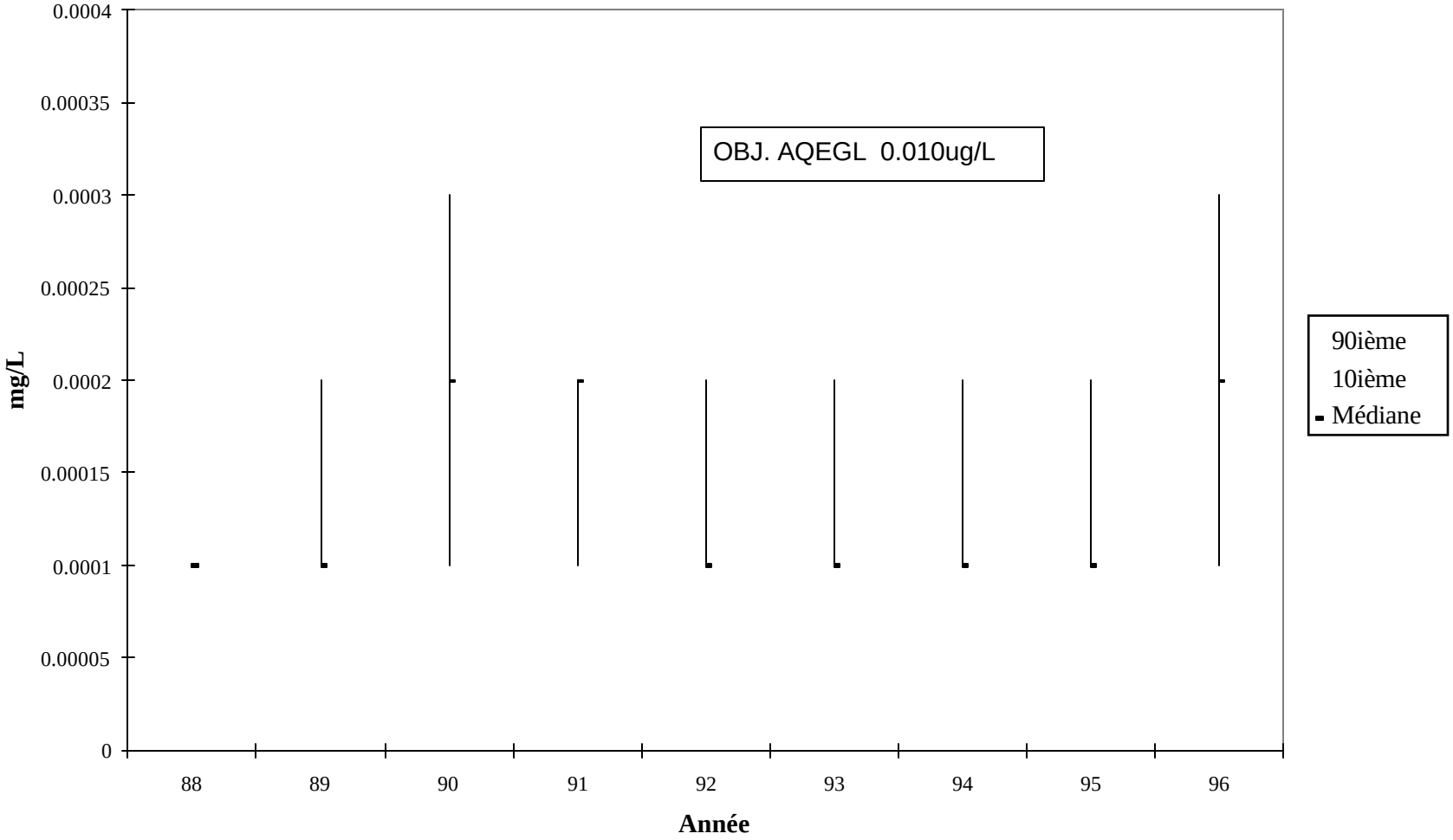
Molybdène total



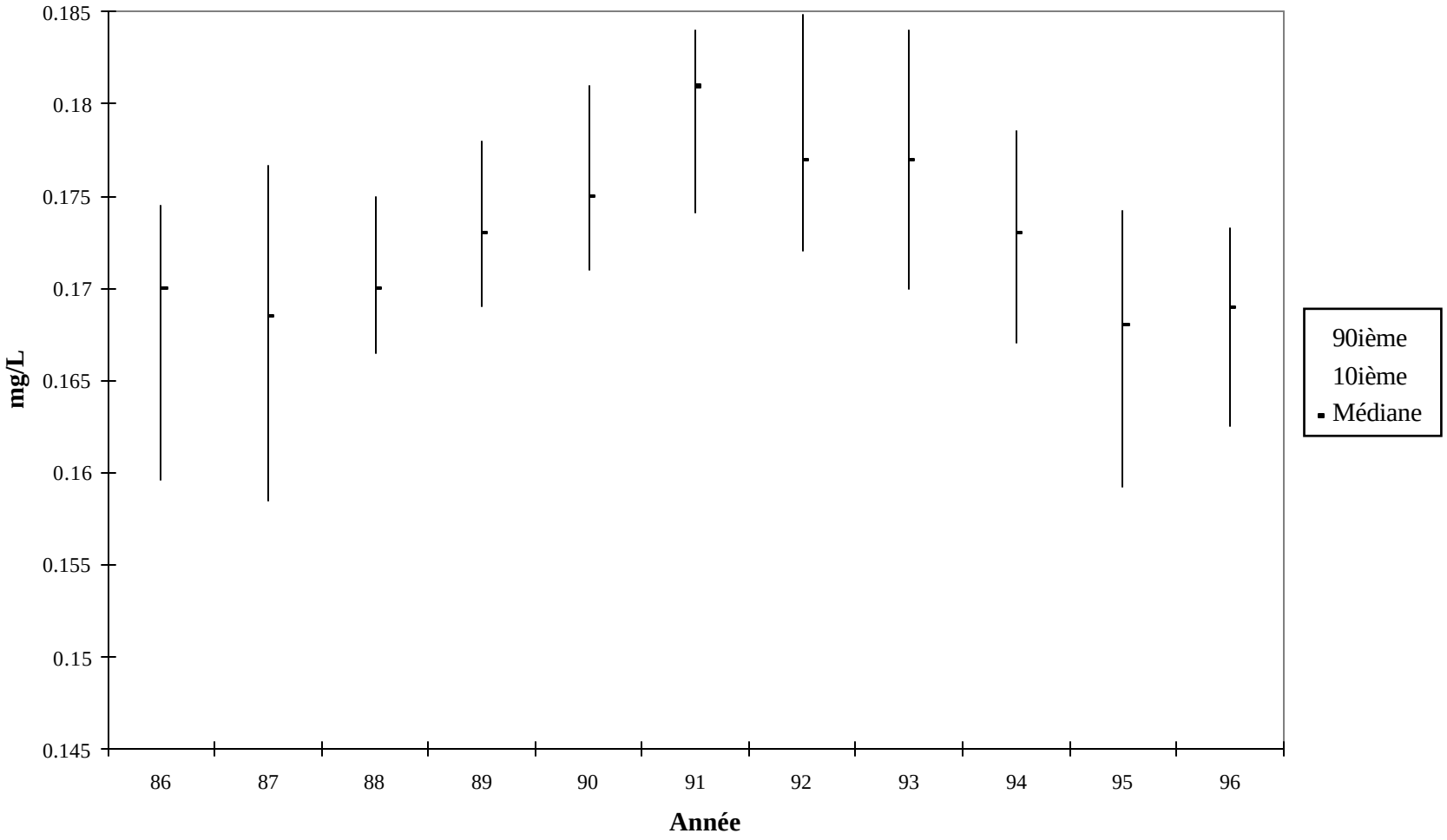
Nickel total



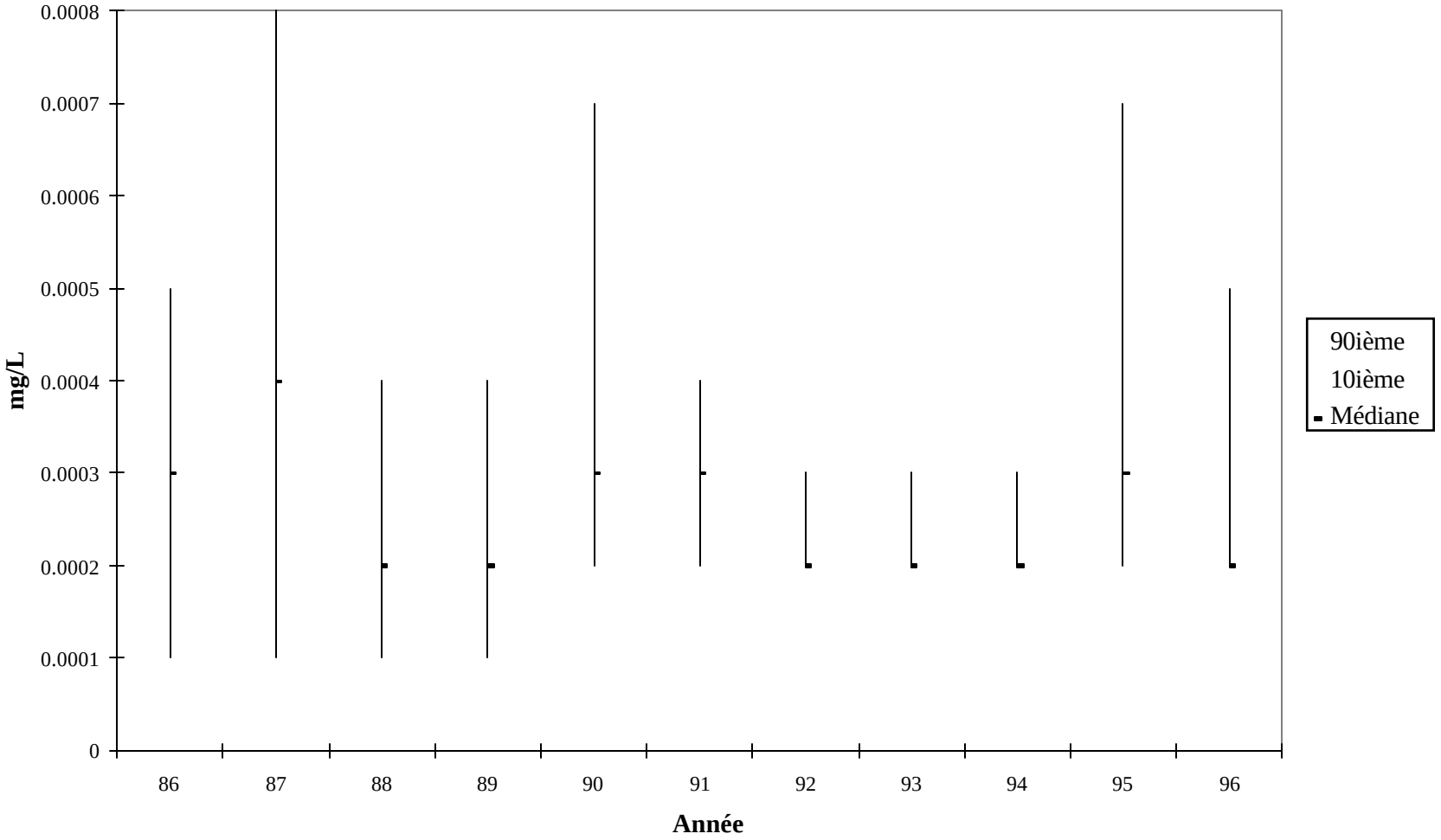
Sélénium total



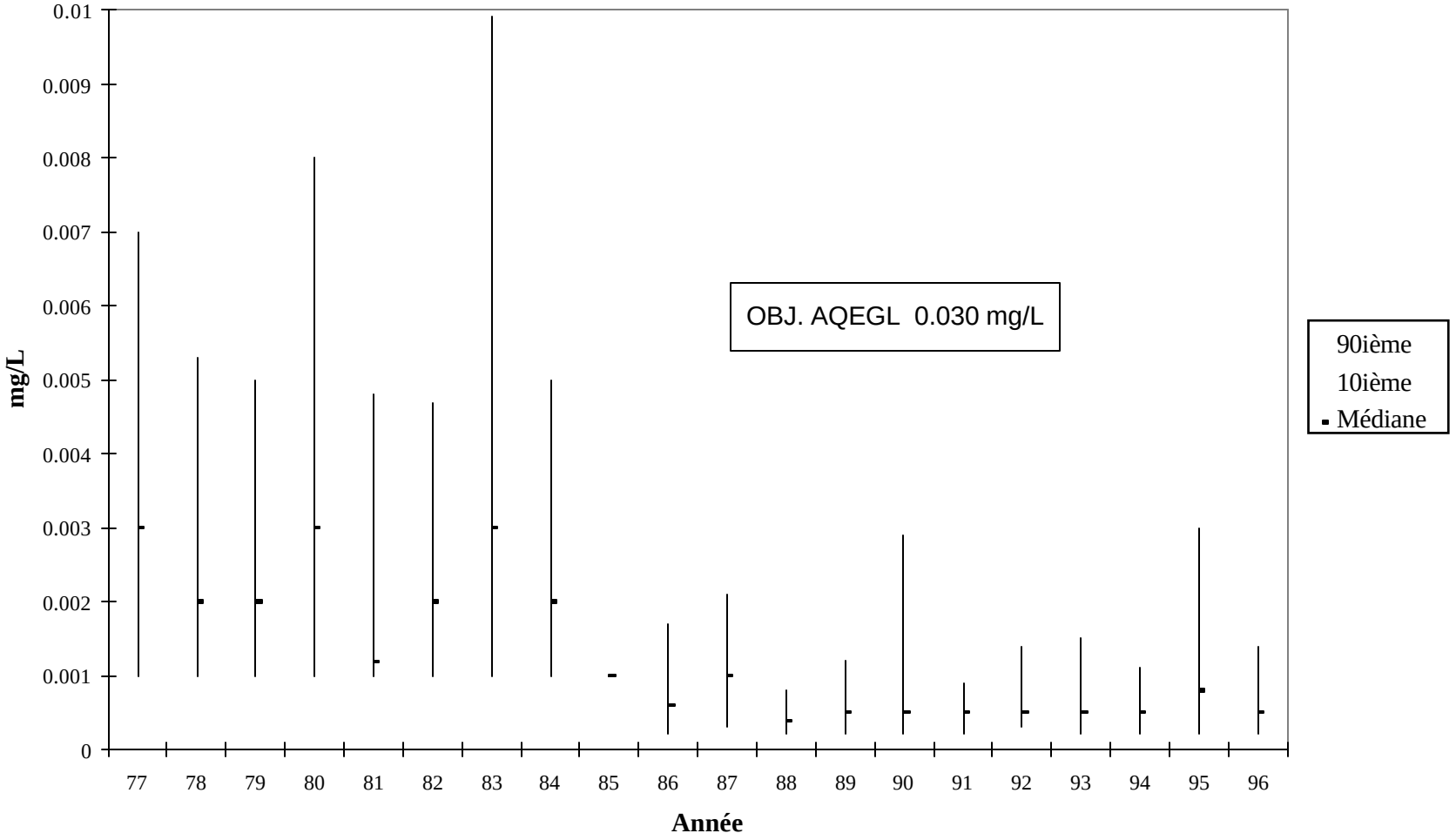
Strontium total



Vanadium total



Zinc total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0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
mg/L
OBJ. AQEGL 0.030 mg/L
90ième
10ième
Médiane
77
78
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80
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86
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88
89
90
91
92
93
94
95
96
Année