

Differences in Results of Analyses of Concurrent and Split Stream-Water Samples Collected and Analyzed by the U.S. Geological Survey and the Illinois Environmental Protection Agency, 1985–91

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 94-4141

Prepared in cooperation with the

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY



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By Charles S. Melching *and* Richard H. Coupe

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CONVERSION FACTORS AND ABBREVIATED WATER-QUALITY UNITS

	Multiply	By	To obtain
	foot per second (ft/s)	0.3048	meter per second
	liter (L)	0.2642	gallon
	liter (L)	33.82	ounce, fluid
	millimeter (mm)	0.03937	inch

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Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by use of the following equation:

$$^{\circ}\text{F} = 1.8(^{\circ}\text{C}) + 32$$

Concentrations are given in milligrams per liter (mg/L) or micrograms per liter (µg/L). For concentrations reported here, milligrams per liter are equivalent to parts per million and micrograms per liter are equivalent to parts per billion.

Differences in Results of Analyses of Concurrent and Split Stream-Water Samples Collected and Analyzed by the U.S. Geological Survey and the Illinois Environmental Protection Agency, 1985–91

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Abstract

During water years 1985-91, the U.S. Geological Survey (USGS) and the Illinois Environmental Protection Agency (IEPA) cooperated in the collection and analysis of concurrent and split stream-water samples from selected sites in Illinois. Concurrent samples were collected independently by field personnel from each agency at the same time and sent to the IEPA laboratory, whereas the split samples were collected by USGS field personnel and divided into aliquots that were sent to each agency's laboratory for analysis. The water-quality data from these programs were examined by means of the Wilcoxon signed ranks test to identify statistically significant differences between results of the USGS and IEPA analyses. The data sets for constituents and properties identified by the Wilcoxon test as having significant differences were further examined by use of the paired t-test, mean relative percentage difference, and scattergrams to determine if the differences were important.

Of the 63 constituents and properties in the concurrent-sample analysis, differences in only 2 (pH and ammonia) were statistically significant and large enough to concern water-quality engineers and planners. Of the 27 constituents and properties in the split-sample analysis, differences in 9 (turbidity, dissolved potassium, ammonia, total phosphorus, dissolved aluminum, dissolved barium, dissolved iron, dissolved manganese, and dissolved nickel) were statistically significant and

large enough to concern water-quality engineers and planners.

The differences in concentration between pairs of the concurrent samples were compared to the precision of the laboratory or field method used. The differences in concentration between pairs of split samples were compared to the precision of the laboratory method used and the interlaboratory precision of measuring a given concentration or property. Consideration of method precision indicated that differences between concurrent samples were insignificant for all concentrations and properties except pH, and that differences between split samples were significant for all concentrations and properties. Consideration of interlaboratory precision indicated that the differences between the split samples were not unusually large. The results for the split samples illustrate the difficulty in obtaining comparable and accurate water-quality data.

INTRODUCTION

The quality of water in a stream is commonly judged by measurements of constituents and properties of the stream water. Such measurements are used to evaluate the stream as (1) a source of drinking water, (2) a habitat for aquatic life, or (3) a place for recreation. Streams are an integral part of the economy and landscape of a community; therefore, the accurate assessment of the quality of water is important. Unbiased and precise measurement of physical properties and constituent concentrations of stream water is difficult and can be affected by the methods

of sample collection, handling, and preservation and by the accuracy of the methods of analysis applied at a given laboratory.

In Illinois, agencies that collect water-quality information include the U.S. Geological Survey (USGS), the U.S. Army Corps of Engineers, the Illinois State Water Survey, and the Illinois Environmental Protection Agency (IEPA). These agencies use either their own or contract laboratories for analysis of water samples, follow specific protocols for sample collection, and generate water-quality data that can be used to evaluate water resources within Illinois.

In most cases, there is little basis for evaluating and comparing data from different agencies to determine whether or how differences in laboratories and methods affect the data; however, the USGS has data that allow USGS and IEPA field-data collection and laboratories to be compared. In 1993, the USGS, in cooperation with IEPA, began a study to compare 7 years of water-quality data for the Illinois Ambient Water-Quality-Monitoring Network (AWQMN). During the years represented by the data (1985-91), samples were collected and analyzed by the USGS and the IEPA and were examined for quality assurance by the USGS. Since 1962, the USGS has done quality assurance of its water-quality data through the Standard Reference Sample Analytical Evaluation Program (SRSAEP) described by Long and Farrar (1992). The USGS and IEPA laboratories are generally rated "good" to "excellent" for most determinations of water-quality constituents; thus, any differences in results from these laboratories for identical or nearly identical samples would be indicative of the difficulties in obtaining consistent and accurate water-quality data for planning and decision making.

The purpose of this report is to describe differences between analytical results for pairs of (1) concurrent samples collected by field personnel of the USGS and the IEPA and (2) split samples—samples divided into replicates at the time and place of sampling—analyzed by the USGS National Water Quality Laboratory (NWQL) and the IEPA laboratories. The data were collected during water years¹ 1985-91 (October 1984 through September 1991).

The report details the results of a stepwise analysis of the concurrent and split samples. The Wilcoxon signed ranks test was used to identify the constituents and properties for which USGS and

IEPA results differed significantly. The constituents and properties so identified were further examined by use of the paired t-test, mean relative percentage difference, and scattergrams to determine if the differences are large enough to affect the usefulness of the data. The differences in results for the concurrent samples were also compared to the precision of the laboratory or field method used for the constituents and properties for which precision data are available. The differences in results for the split samples were also compared to the precision of the laboratory method used and to the interlaboratory precision of determining a given constituent or property for the constituents and properties for which precision data are available. Mean relative percentage differences greater than 10 percent, high scatter of the data relative to the line of perfect agreement (1:1) for IEPA and USGS results, or large ratios between the concentration difference and the standard deviation resulting from method precision indicate differences in concentrations or properties are large enough to concern water-quality engineers and planners.

COLLECTION AND ANALYSIS OF CONCURRENT AND SPLIT SAMPLES

A water-quality sampling program consists of three principal aspects: site selection, sample-collection techniques, and laboratory procedures. Each of these aspects of the concurrent- and split-sampling programs are briefly discussed following a short history and description of the sampling programs.

History and Description of the Sampling Programs

The USGS and the IEPA cooperatively operated the Illinois AWQMN during water years 1978-92. (IEPA continues to operate the AWQMN without USGS involvement.) The AWQMN consists of approximately 208 water-quality stations on streams throughout Illinois, including 7 National Stream-Quality Accounting Network (NASQAN) stations monitored by USGS personnel. USGS personnel collected samples at about 20 of the stations and provided discharge data for most of the other stations; IEPA personnel collected samples at the remainder of the stations. IEPA field personnel were trained by USGS personnel at the beginning of the cooperative program. IEPA personnel use USGS-approved field methods (Edwards and Glysson, 1988) except at times of equipment limitations. The field and laboratory

¹The water year is the 12-month period from October 1 through September 30 and is designated by the calendar year in which it ends and which includes 9 of the 12 months.

data were stored in the USGS National Water Information System (NWIS), in the National Water Data Storage and Retrieval System (WATSTORE), and in the U.S. Environmental Protection Agency Storage and Retrieval System (STORET) through September 1992. The data were also published in the USGS annual water-data reports for Illinois from 1985 to 1991; for example, the data for water year 1991 is listed in Maurer and others (1992) and Richards and others (1992).

As a part of the USGS quality-assurance program in Illinois, concurrent samples (collected independently by field personnel from each agency at the same time) and split samples (collected by USGS field personnel and from which aliquots were sent to each agency's laboratory for analysis) were collected at selected sites during water years 1985–91. Concurrent samples were collected twice annually, spring and fall, at the seven NASQAN stations included in the AWQMN. In water years 1985–87, additional sites were selected for sampling. After 1987, budgetary constraints reduced the concurrent sampling program to only the NASQAN stations. Water samples were routinely collected by USGS personnel at each NASQAN station four to six times a year, and aliquots were processed in accordance with instructions for the NASQAN and IEPA programs.

Sites

The stations at which the concurrent- and split-sample data were collected are located throughout the State and represent various types of stream water in Illinois. The locations of the NASQAN stations and the AWQMN stations used in the comparison of concurrent and split samples are shown in figure 1. Samples were collected to represent a range of flow and water quality.

Constituents and Properties Examined

The constituents and properties analyzed for and mentioned in this report are those in the protocols for each of the networks. For the AWQMN, the basic set of constituents is the same throughout the State; however, certain constituents are determined at some stations and not at others. In the split-sample program, the NASQAN and AWQMN protocols include the major nutrients, cations, anions, and field-measured constituents and properties in common; but for the trace metals, the NASQAN protocol includes only dissolved metals.

Techniques of Sample Collection

USGS personnel used a depth-integrating sampler that was appropriate for the flow at the time of sampling (Edwards and Glysson, 1988). In the USGS procedure, a weighted-bottle sampler is used for velocities less than 2.0 ft/s, and depth-integrating samplers are used for velocities equal to or greater than 2.0 ft/s. In Illinois, however, the USGS has set 1.5 ft/s as the dividing line between the use of weighted-bottle and depth-integrating samplers.

IEPA used weighted-bottle samplers and DH-48 and DH-76 depth-integrating samplers. The IEPA used weighted-bottle samplers for flow velocities less than 2.0 ft/s and depth-integrating samplers for flow velocities between 2.0 and 4.0 ft/s. The weighted-bottle sampler may also have been used at flow velocities greater than 4.0 ft/s because the IEPA did not have heavy sampling equipment that they considered appropriate for these flow velocities.²

Concurrent samples were collected with separate equipment and were composited in separate churn splitters. Identical measurement techniques were used by the USGS and the IEPA when the available equipment was comparable. Both samples were put into bottles obtained from the IEPA laboratory. Preservatives were added to the bottles by IEPA lab personnel before the bottles were taken to the field. Samples were chilled and were usually taken to the IEPA laboratory on the day of collection.

Water for split samples was collected by USGS personnel and was composited in a churn splitter. Aliquots were taken from the churn splitter, filtered separately by each agency with 142-mm plate filters, and preserved in accordance with the instructions for each of the water-quality networks. Preservatives, if necessary, were added to the bottles used at NASQAN stations in the field. Field measurements from concurrent samples (pH, water temperature, specific conductance, and dissolved oxygen) were made by field personnel from both agencies at the same time and at the center of flow. Hydrolab Model 4041³ four-parameter meters were generally used. Other meter types were used if the Hydrolab meter malfunctioned. Results were recorded on a field form.

²Edwards and Glysson (1988, p. 8) report the maximum velocities for DH-48 and DH-76 depth-integrating samplers are 8.86 and 6.6 ft/s, respectively.

³Use of firm or trade names in this report is for identification only and does not constitute endorsement by the U.S. Geological Survey.

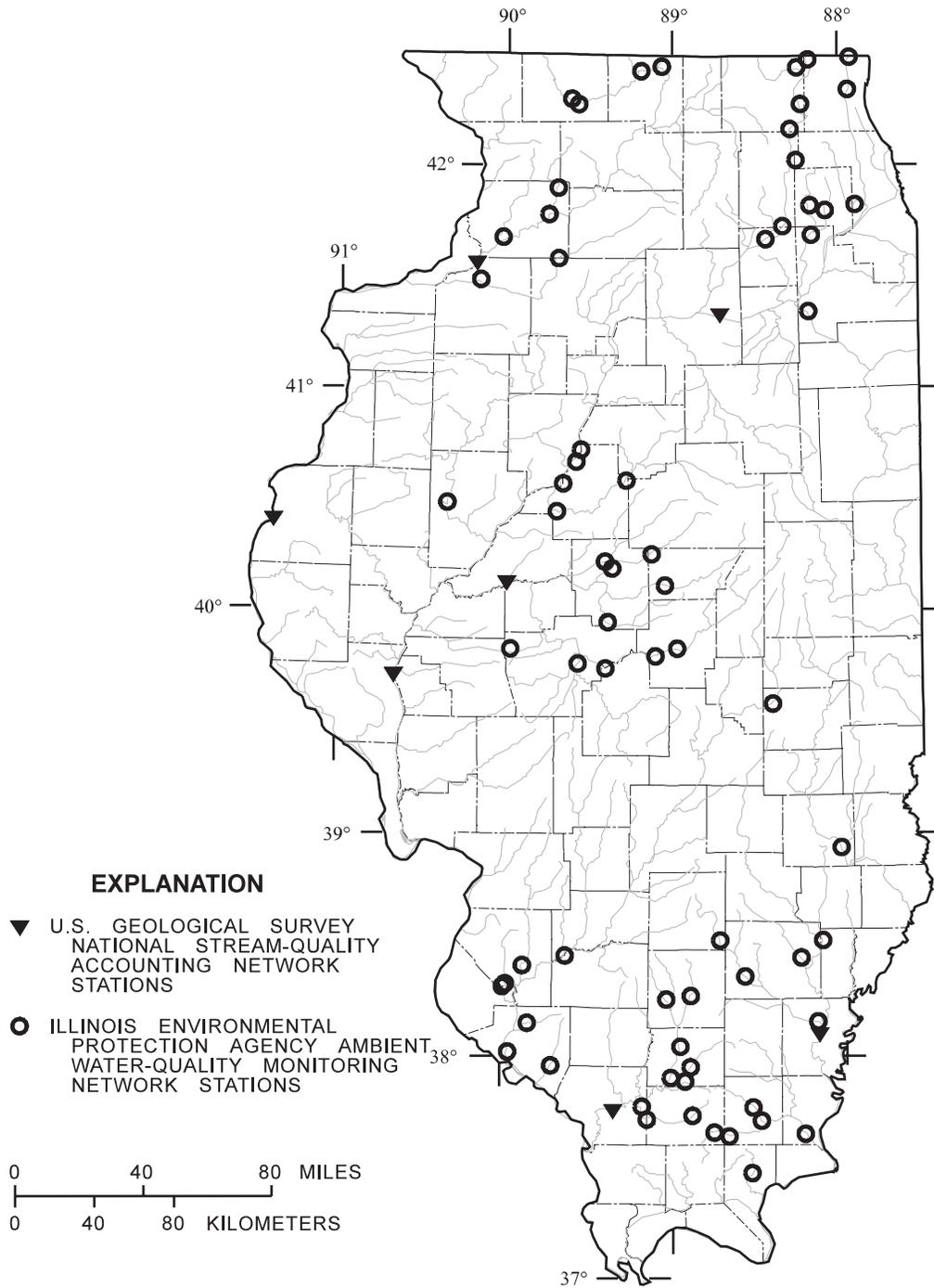


Figure 1. Locations of water-quality stations in Illinois where concurrent and (or) split samples of stream water were collected.

Sample Handling and Preservation

Sample handling and preservation refer to procedures used to prevent changes in the chemical, physical, and (or) biological characteristics of a sample with time. These procedures may differ among constituents and may include limits on holding time (the time between sample collection and analysis), types of containers, and sample preservation. For the concurrent data, handling and preservation procedures for the two agencies were identical because the water samples were sent to the IEPA laboratory for analysis. For the split samples use of preservatives, holding times, and containers was variable. A split sample sent to different laboratories will usually result in greater differences than if the samples were sent to the same laboratory because between laboratory differences usually are greater than within laboratory differences. Finally, different laboratory measurement techniques almost always produce variable results because of how the interactions among chemical constituents (matrix effects) affect the laboratory measurement techniques.

Laboratory Procedures

Most of the analyses of water samples collected in the concurrent-sampling program and those (IEPA samples) collected in the split-sampling program were done at the IEPA laboratory in Champaign or Chicago, Ill. Analyses included determinations of nutrients, chemical oxygen demand (COD), sulfate, chloride, fluoride, and total and dissolved solids. Concentrations of trace metals were measured at the Champaign laboratory using the inductively coupled plasma (ICP) method described by Fishman and Friedman (1989). All methods (except the ICP method) are documented in the method manual for the IEPA laboratory (Illinois Environmental Protection Agency, 1987a and b). NASQAN samples were sent to the NWQL in Arvada, Colo., for analyses described in Fishman and Friedman (1989) and Fishman (1993).

DIFFERENCES IN ANALYTICAL RESULTS

The statistical analysis and data-handling procedures used in this study were nearly identical for the concurrent- and split-sample data sets. The statistical procedures and results for the concurrent samples and the laboratory analysis of split samples are described in the following sections.

Statistical Tests

In the comparison of results from the USGS and IEPA concurrent water-quality samples and the USGS and IEPA laboratory analysis of split water-quality samples, two statistical tests were done in a stepwise manner. The Wilcoxon signed ranks test (Conover, 1980, p. 278–292) was used to determine whether differences between constituent concentrations or other measurements determined for the USGS and IEPA concurrent or split samples were statistically significant. In the Wilcoxon signed ranks test (and the paired t-test discussed later), the hypothesis examined is that the central values of the data series do not differ. For a two-sided Wilcoxon signed ranks test, the critical value of the test statistic above which (in absolute value) the hypothesis can be rejected is 1.96 at the 5-percent level of significance, α , and 2.5758 at the 1-percent level of significance. These critical values are based on a normal distribution approximation that should be accurate because data for all the constituents and properties of interest consisted of more than 30 sample pairs (Helsel and Hirsch, 1992, p. 104). The α indicates the probability of rejecting the hypothesis when it is in fact true.

The Wilcoxon signed ranks test has been successfully applied to determine whether differences in paired data are significant where the differences between the paired data are symmetrically distributed. The Wilcoxon signed ranks test is robust in analyzing the mean or median of symmetrically distributed data. For example, its absolute efficiency is 86.4 percent relative to the paired t-test for normally distributed data (for which the paired t-test is most powerful), and it has much higher efficiency than that of the paired t-test for some data that are not normally distributed (Conover, 1980, p. 291). The flexibility and efficiency of the Wilcoxon signed ranks test have made it popular for detecting differences in the mean or median of water-quality data. For example, Ward and others (1988) recommend the use of the Wilcoxon signed ranks test for analysis of ground-water-quality data.

The Wilcoxon signed ranks test is a weighted version of the sign test (Conover, 1980, p. 122–129) where the rankings of the differences are used as the weighting factors. The test has two major limitations in determining whether differences between paired data sets are important from a practical point of view. First, the rankings do not account for the magnitude of the differences between the data series. For example, given paired data where the difference between the data is 1 percent for all cases, the test result would be the same as that for paired data where the difference between the data is 50 percent for all cases. Second,

the test does not consider pairs where the difference is 0. Thus, if a large percentage of the data pairs were equal, this perfect agreement between the data series would not be considered in the test. As detailed later in the sections "Differences Between Pairs of Concurrent Samples" and "Differences Between Pairs of Split Samples," greater than 40 percent of the data pairs were equal for 37 of 63 (59 percent) constituents and 11 of 27 (41 percent) constituents, respectively.

The constituents and properties for which the Wilcoxon signed ranks test indicated significant differences between the samples or laboratory analyses were further examined in four ways to consider if the magnitude of the differences was important from a practical point of view. The data were analyzed by use of the paired t-test (Conover, 1980, p. 290) to evaluate the magnitude of the difference in means relative to the variance of the differences. The mean relative percentage difference, RPD, also was computed for each constituent or property as

$$RPD = \frac{\sum_{i=1}^N [2(C_{USGSi} - C_{IEPAi}) / (C_{USGSi} + C_{IEPAi})]}{N}, \quad (1)$$

where C_{USGSi} is the constituent concentration or other measurement determined by the USGS for data pair i , C_{IEPAi} is the constituent concentration or other measurement determined by IEPA for data pair i , and N is the number of sample pairs. Scattergrams of the paired USGS and IEPA constituent concentrations or other measurements were prepared, and the distribution of the data relative to the perfect-agreement (1:1) line was observed. Finally, the differences in concentration for the concurrent samples were compared to available information on the precision of the laboratory or field method used. The differences in concentration for the split samples were compared to available information on the precision of the laboratory method used and the interlaboratory precision of determining a given constituent. Low scatter of the data relative to the perfect-agreement line, RPD values less than 10 percent, and ratios of less than 2 between differences in constituent concentrations and the standard deviation resulting from method precision indicate the difference between USGS and IEPA data were not important from a practical point of view.

Consideration of Method Detection Limits

For many of the samples measured or analyzed jointly by the USGS and IEPA, the concentration of the constituent was less than the method detection limit (MDL) of the laboratory analysis. A common approach in statistical analysis of water-quality data is to set the concentration equal to one-half of the MDL and continue with the statistical analysis (Ward and others, 1990, p. 105). The midpoint is selected because the mean of the observations remains unbiased as long as all measurements between 0 and the MDL are equally probable and are uniformly distributed (Gilbert, 1987, p. 178). This procedure was used where the USGS and IEPA measurements were at or below the same MDL and where the concentration in one sample was below the MDL, whereas the concentration in the other sample exceeded the MDL.

In the comparison of USGS and IEPA split samples, the MDL for IEPA analyses was much higher than the MDL for USGS analyses for many of the constituents. Thus, many constituent concentrations reported by the USGS were below the IEPA MDL's for those same constituents. Further, several unequal MDL's were found in the comparison of concurrent USGS and IEPA samples even though the IEPA laboratory analyzed both samples. If MDL's are unequal or if they change over time as more sensitive instruments are developed, Hirsch and others (1982) recommend that all data reported as less than the highest MDL (including those reported as less than any lower MDL) be considered to be tied at the highest MDL. This recommendation is reasonable for the comparisons of samples or of laboratory analyses herein because the concentrations were in agreement to the accuracy available.

All data less than the highest MDL were considered to be tied at the highest MDL in the comparison of concurrent water-quality samples, and the ties derived in this manner were deleted from all the statistical comparisons used. For the comparison of split water-quality samples, all data less than the highest MDL were considered to be tied at the highest MDL and were deleted from the Wilcoxon signed ranks test. The t-test and the RPD calculations, however, were done by means of two approaches where the USGS concentration was greater than the USGS MDL but less than the IEPA MDL: (1) Data were considered to be tied at the highest MDL and were deleted and (2) USGS concentrations were used as reported and IEPA concentrations were set to one-half of the IEPA MDL. The scattergrams were plotted for the second approach. All ties where both USGS and IEPA concentrations were less than the

respective, nonequal MDL's were deleted from the tests and the scattergrams.

Differences Between Pairs of Concurrent Samples

Constituent concentrations and other measurements that were significantly different between USGS and IEPA samples were identified by use of the Wilcoxon signed ranks test as described below. Also described is the further comparison of these data to evaluate the differences from a practical point of view with the paired t-test, RPD, scattergrams, and comparison with the standard deviation resulting from the precision of the laboratory or field method used.

Results of Wilcoxon Signed Ranks Test

The Wilcoxon test statistic and the types of sample pairs available in the concurrent-sampling data are listed in table 1. The hypothesis of no difference

between the central values of the sample pairs can be rejected (1) at the 1-percent significance level for pH, dissolved oxygen, dissolved magnesium, ammonia, and dissolved barium; and (2) at the 5-percent significance level for dissolved calcium, dissolved sodium, total lead, dissolved zinc, and total cyanide. Concentrations and other measurements in the samples collected by the USGS tend to be higher than those in the samples collected by the IEPA for all the water-quality constituents for which a significant difference was detected. The test results may not be appropriate for total lead, dissolved zinc, and total cyanide because nonzero differences were found for only 18 of 151, 11 of 144, and 5 of 89 sample pairs, respectively. Further, the number of sample pairs with zero difference ranged from 25 to 66 for the other constituents and properties judged significantly different by use of the Wilcoxon signed ranks test. The large number of sample pairs with zero difference illustrate the need for use of the paired t-test, RPD, and scattergrams to

Table 1. Results of Wilcoxon signed ranks test of differences between U.S. Geological Survey and Illinois Environmental Protection Agency concurrent samples of water from Illinois streams
[MDL, method detection limit; <, less than; °C, degrees Celsius]

Constituent or property	Num ber of pairs of samples with one sample <MDL ¹	Num ber of pairs of samples with both samples <MDL ¹	Number of sample pairs	Number of nonzero differences ²	Wilcoxon statistic ³
Specific conductance	0	0	145	133	-0.682
pH	0	0	132	107	-5.810
Temperature	0	0	145	47	-1.620
Turbidity	1(1)	0	132	121	-.635
Dissolved oxygen	0	0	145	120	-3.285
Chemical oxygen demand (low level)	0	0	143	117	-.904
Calcium, total	0	0	151	103	-.785
Calcium, dissolved	0	0	145	116	-2.507
Magnesium, total	0	0	151	72	-.601
Magnesium, dissolved	0	0	146	91	-2.923
Sodium, total	0	0	151	81	-.589
Sodium, dissolved	0	0	146	101	-2.267
Potassium, total	1	0	148	108	1.224
Potassium, dissolved	1	0	143	125	-1.123
Alkalinity	2	4	105	78	.926
Chloride	0	0	103	49	1.827
Fluoride, total	1	1	82	20	-.282
Residue, total at 105°C	0	0	152	136	-.089
Residue volatile	2	0	152	121	-.329
Nitrite plus nitrate	5	9	148	87	-.184
Ammonia	12(1)	51	149	83	-2.959
Organic nitrogen	0	0	64	49	-.617

Table 1. Results of Wilcoxon signed ranks test of differences between U.S. Geological Survey and Illinois Environmental Protection Agency concurrent samples of water from Illinois streams—Continued

Constituent or property	Num	Num	Number of sample pairs	Number of nonzero differences ²	Wilcoxon statistic ³
	ber of pairs of samples with one sample <MDL ¹	ber of pairs of samples with both samples <MDL ¹			
Ammonia + organic nitrogen	0	0	96	68	-1.248
Nitrogen, total	0	0	90	72	-1.143
Phosphorus, total	1	1	149	103	-.105
Phosphorus, dissolved	3(2)	5	140	90	-0.568
Aluminum, total	1	1	151	125	-.049
Aluminum, dissolved	49	70	145	70	-1.379
Arsenic, total	0	8	81	21	1.337
Barium, total	0	0	151	25	1.688
Barium, dissolved	0	0	146	121	-3.502
Beryllium, total	2	141(16)	151	7	-.938
Beryllium, dissolved	0	129(15)	146	1	-1.000
Boron, total	10	64	151	48	.868
Boron, dissolved	7	64	136	45	.324
Cadmium, total	18(4)	126	149	20	1.210
Cadmium, dissolved	15(1)	127(3)	144	16	.183
Chromium, total	45	74	151	75	-1.214
Chromium, dissolved	23	113(1)	145	30	.928
Cobalt, total	32	103	151	43	-.430
Cobalt, dissolved	16	120(2)	142	21	1.014
Copper, total	50	60	150	87	-.693
Copper, dissolved	33	100(1)	141	41	1.177
Iron, total	1	0	154	120	.653
Iron, dissolved	38	84	145	60	-.688
Lead, total	12	132(15)	151	18	-2.310
Lead, dissolved	2	143(11)	145	4	-1.826
Manganese, total	0	0	151	116	-.196
Manganese, dissolved	17	9	145	109	-1.464
Nickel, total	45	54(1)	150	91	-.867
Nickel, dissolved	48	70(6)	143	73	1.522
Silver, total	29	111	151	40	-.473
Silver, dissolved	29	112(3)	143	30	1.891
Strontium, total	0	0	151	50	-.136
Strontium, dissolved	0	0	144	77	-1.612
Vanadium, total	37	79(1)	151	70	.766
Vanadium, dissolved	21	122(1)	145	22	1.452
Zinc, total	13	130(24)	151	21	-1.096
Zinc, dissolved	7	133(17)	144	11	-1.961
Carbon, organic total	0	0	36	34	1.531
Cyanide, total	2	77	89	5	-2.060
Phenols, total	9	72	87	12	-1.272
Oil and grease	18	6	92	47	-.859

¹Numbers in parentheses indicate number of pairs with unequal MDL's; for the case with one sample less than the MDL, this indicates the second sample in the pair is less than the MDL for the first sample.

Zero differences include all pairs where both concentrations or measurements are the same or less than their MDL's, or where each concentration or measurement is below the less restrictive of the MDL's.

Negative values indicate that U.S. Geological Survey samples tend to have higher concentrations or other measurements than Illinois Environmental Protection Agency samples.

describe the magnitude of differences between the samples.

Results of Paired t-test

Listed in table 2 are the number of sample pairs considered, Student's t, the critical bounds on t for

Table 2. Results of paired t-test and relative percentage difference analysis for the U.S. Geological Survey and Illinois Environmental Protection Agency concurrent samples of water from Illinois streams [RPD, relative percentage difference; α , statistical significance level]

Constituent or property	Number of sample pairs	Student's t^1	Bound on t statistic		Mean RPD (percent)
			$\alpha = 0.05$	$\alpha = 0.01$	
pH	132	-6.68	1.98	2.62	² 3.51
Dissolved oxygen	145	-2.77	1.98	2.62	4.13
Calcium, dissolved	145	-1.79	1.98	2.62	4.53
Magnesium, dissolved	146	-.574	1.98	2.62	4.61
Sodium, dissolved	146	-1.20	1.98	2.62	5.24
Ammonia	149	-2.75	1.98	2.62	25.7
Barium, dissolved	146	-2.70	1.98	2.62	7.19
Lead, total	136	-.316	1.98	2.62	12.8
Zinc, dissolved	127	-2.33	1.98	2.62	8.41
Cyanide, total	89	-2.12	1.99	2.64	7.55

¹Negative values indicate that U.S. Geological Survey samples tend to have higher pH or constituent concentrations than Illinois Environmental Protection Agency samples.

$\alpha = 0.05$ and $\alpha = 0.01$, and the mean RPD. The hypothesis of no difference between the central values of the samples can be rejected (1) at the 1-percent significance level for pH, dissolved oxygen, ammonia, and dissolved barium; and (2) at the 5-percent significance level for dissolved zinc and total cyanide. The hypothesis of no difference between the central values of the samples cannot be rejected at the 5-percent significance level for dissolved calcium, dissolved magnesium, dissolved sodium, and total lead; otherwise, the paired t-test and Wilcoxon signed ranks test lead to identical conclusions.

Relative Percentage Difference and Scatter

The RPD was calculated and the scattergrams were prepared to examine the magnitude of the differences between concentrations and other measurements in the sample pairs. The mean RPD is less than 10 percent for all constituents except ammonia and total lead. For pH, the reporting of the mean is somewhat misleading because pH is a logarithmically scaled variable, and a 10-percent difference in logarithms results in more than 100-percent difference in the hydrogen ion concentration. Scattergrams for the constituents are shown in figures 2–11 (at end of report). Not all data pairs are presented in figures 2–11; extreme concentrations were deleted from the plots so that the scale of the plots allows reasonable assessment of the agreement between the USGS and IEPA concentrations.

The scattergram for pH (fig. 2) shows that the differences in pH between USGS and IEPA samples are substantial given the small range over which pH was measured. The scattergrams for dissolved oxygen, dissolved calcium, dissolved magnesium, dissolved

sodium, and dissolved barium (figs. 3–6 and 8, respectively) indicate considerable agreement between IEPA and USGS concentrations. The wide scatter in the diagram for ammonia (fig. 7) indicates considerable disagreement between the IEPA and USGS concentrations. The scattergrams for total lead, dissolved zinc, and total cyanide (figs. 9–11) depict substantial scatter, but the small number of points, several of which represent many data pairs, preclude judgment of differences between USGS and IEPA samples.

Consideration of Method Precision

The differences between the concentrations of pairs of USGS and IEPA samples can also be evaluated for practical importance in terms of the precision of the methods used by the IEPA laboratory to measure the constituent concentrations. All laboratory analyses and techniques are subject to random errors and uncertainties because of difficulties in preparing and analyzing samples identically and in obtaining reproducible split samples. These random errors are known as the precision of a method. The precision of a method is assessed by analyzing split samples in replicate at the same laboratory under nearly identical conditions and statistically evaluating the results.

Dissolved oxygen and pH were measured in the field by use of a Hydrolab Model 4041 four-parameter meter. The manufacturer reports that the calibrated accuracy of the 4041 meter for dissolved oxygen is ± 0.2 mg/L and for pH is ± 0.1 standard units. The standard deviation resulting from method precision, S_p , is about one-half of the calibrated accuracy. The IEPA laboratory used the ICP method to measure concentrations of dissolved magnesium, dissolved

barium, dissolved calcium, dissolved sodium, and dissolved zinc. For constituents measured by the ICP method, S_p is given as a linear-regression equation where measured concentration is the independent variable (Fishman and Friedman, 1989, p. 522). No information is available on S_p for the laboratory methods used by IEPA to measure concentrations of ammonia, total lead, and total cyanide. The mean and the median of (1) the ratio and (2) the absolute value of the ratio of the difference in concentration between USGS and IEPA samples and S_p are given in table 3. The mean and (or) median is less than or equal to one standard deviation resulting from method precision for all the constituents listed in table 3 except pH; thus, the differences in constituent concentrations are reasonable from a practical point of view. The large mean of the ratio for pH supports the conclusion that the differences in pH between IEPA and USGS measurements are statistically significant and practically important.

Significance of Differences

The results of the statistical tests and other comparisons of the concurrent samples are summarized in table 4. The substantial differences between USGS and IEPA samples for pH and ammonia concentration are evident from the significance level for the statistical tests (table 4) and wide data scatter (figs. 2 and 7, respectively). Differences in concentrations of dissolved oxygen and dissolved barium are statistically significant (rejection at low α values in table 3) but not practically important (low mean RPD; low data scatter in figs. 3 and 8, respectively; and low mean and median ratios to S_p). For dissolved calcium, dissolved magnesium, and dissolved sodium, only the Wilcoxon signed ranks test indicates a significant dif-

ference in the samples; thus, for these constituents the differences in concentration are probably not important from a practical point of view. Total lead, dissolved zinc, and total cyanide concentrations may differ significantly between the paired samples, but the sample sizes for these constituents are too small (table 4) for drawing conclusions. In general, USGS and IEPA field personnel seem to have collected and handled water samples in a comparable and reliable manner.

Differences Between Pairs of Split Samples

Constituent concentrations and other measurements that were significantly different between USGS and IEPA samples were identified by use of the Wilcoxon signed ranks test as described below. Also described is the further comparison of these data to evaluate the differences from a practical point of view with the paired t-test, RPD, scattergrams, and comparison with the standard deviation resulting from the precision of the laboratory method used and resulting from interlaboratory precision.

Results of Wilcoxon Signed Ranks Test

The Wilcoxon test statistic and the types of sample pairs available in the split-sample data are listed in table 5. The hypothesis of no difference between the central values of the sample pairs can be rejected (1) at the 1-percent significance level for turbidity, dissolved sodium, dissolved potassium, ammonia, total phosphorus, dissolved aluminum, dissolved barium, dissolved chromium, dissolved cobalt, and dissolved manganese; and (2) at the 5-percent significance level for alkalinity, chloride, dissolved iron, dissolved nickel, and dissolved silver. With the exception of turbidity, dissolved potassium, and dissolved barium, the measurements made by the IEPA laboratories tend to be higher than those made by the USGS laboratory for all the water-quality constituents for which a significant difference was detected. The test results may not be appropriate for dissolved chromium, dissolved cobalt, dissolved iron, dissolved nickel, and dissolved silver because nonzero differences were found for only 27 of 133, 9 of 134, 51 of 133, 48 of 130, and 7 of 132 sample pairs, respectively.

Table 3. Ratios of differences in concentration between samples of water from Illinois streams collected by the U.S. Geological Survey and Illinois Environmental Protection Agency and the standard deviation resulting from method precision

Constituent or property	Ratio		Absolute value of the ratio	
	Mean	Median	Mean	Median
pH	3.73	2.00	5.33	4.00
Dissolved oxygen	1.24	1.00	3.41	2.00
Magnesium, dissolved	1.87	.00	6.38	4.47
Barium, dissolved	1.70	.86	2.96	1.73
Calcium, dissolved	.96	1.50	4.17	2.05

Table 4. Summary of statistical-test results and other analyses of U.S. Geological Survey and Illinois Environmental Protection Agency concurrent samples of water from Illinois streams [RPD, relative percentage difference; MDL, method detection limit; N.A., not applicable; --, not determined]

Constituent or property	Significance level for given test		Mean RPD (percent)	Amount of scatter about 1:1 line	Sample pairs where both concentrations exceeded greatest MDL
	Wilcoxon signed ranks	Paired t-test			
pH	0.01	0.01	3.51	High	N.A.
Oxygen, dissolved	.01	.01	4.13	Low	N.A.
Calcium, dissolved	.05	--	4.53	Low	145
Magnesium, dissolved	.01	--	4.61	Low	146
Sodium, dissolved	.05	--	5.24	Low	146
Ammonia	.01	.01	25.7	High	97
Barium, dissolved	.01	.01	7.19	Low	146
Lead, total	.05	--	12.8	High	19
Zinc, dissolved	.05	.05	8.41	High	11
Cyanide, total	.05	.05	7.55	High	12

Table 5. Results of Wilcoxon signed ranks test of differences between U.S. Geological Survey and Illinois Environmental Protection Agency split samples of water from Illinois streams [MDL, method detection limit; <, less than]

Constituent or property	Number of pairs of samples with one sample < MDL ¹	Number of pairs of samples with both samples < MDL ¹	Number of sample pairs	Number of nonzero differences ²	Wilcoxon statistic ³
Turbidity	0	0	160	158	-6.503
Calcium, dissolved	0	0	191	160	.703
Magne- sium, dissolved	0	0	192	142	1.420
Sodium, dissolved	0	0	189	159	3.042
Potassium, dissolved	1	0	192	178	7.006
Alkalinity	3	0	142	138	-2.429
Sulfate	0	0	151	132	1.693
Chloride	0	0	152	125	2.147
Nitrite plus nitrate	9(1)	13(1)	177	142	.256
Ammonia	61(45)	7(7)	170	113	4.467
Phospho- rus, total	0	0	177	165	4.057
Phospho- rus, dissolved	3	0	171	138	1.780
Aluminum, dissolved	48(21)	29(29)	130	79	4.908
Barium, dissolved	0	0	132	119	-5.813
Beryllium, dissolved	10(1)	124(123)	134	9	-6.53
Cadmium, dissolved	39(29)	90(89)	133	14	1.424

Table 5. Results of Wilcoxon signed ranks test of differences between U.S. Geological Survey and Illinois Environmental Protection Agency split samples of water from Illinois streams
[MDL, method detection limit; <, less than]

Constituent or property	Number of pairs of samples with one sample < MDL ¹	Number of pairs of samples with both samples < MDL ¹	Number of sample pairs	Number of nonzero differences ²	Wilcoxon statistic ³
Chromium, dissolved	38(15)	90(85)	132	27	4.058
Cobalt, dissolved	1(1)	124(124)	134	9	2.692
Copper, dissolved	88(76)	17(17)	130	33	1.022
Iron, dissolved	83(74)	7(7)	133	51	2.068
Lead, dissolved	32(27)	99(75)	132	6	-.530
Manganese, dissolved	11(5)	4(4)	132	106	3.639
Nickel, dissolved	78(63)	19(19)	130	48	2.553
Silver, dissolved	22(15)	110(110)	132	7	2.387
Strontium, dissolved	0	0	127	92	-.366
Vanadium, dissolved	12(1)	122(122)	134	11	1.309
Zinc, dissolved	15(114)	12(12)	132	6	.943

¹Numbers in parentheses indicate number of pairs with unequal MDL's; for the case with one sample less than the MDL, this indicates the second sample in the pair is less than the MDL for the first sample.

²Zero differences include all pairs where both concentrations or measurements are the same or less than their MDL's, or where each concentration or measurement is below the less restrictive of the MDL's.

³Negative values indicate that U.S. Geological Survey samples tend to have higher concentrations or other measurements than Illinois Environmental Protection Agency samples.

Results of Paired t-test

Listed in table 6 are the number of sample pairs considered, Student's t, the critical bounds on t for $\alpha = 0.05$ and $\alpha = 0.01$, and the mean RPD. The hypothesis of no difference between the central values of the samples can be rejected (1) at the 1-percent significance level for turbidity, dissolved sodium, dissolved potassium, ammonia, total phosphorus, dissolved barium, dissolved chromium, dissolved cobalt, dissolved nickel, and dissolved silver; and (2) at the 5-percent significance level for dissolved aluminum and dissolved manganese. The hypothesis of no difference between the central values of the samples cannot be rejected at the 5-percent significance level for alkalinity, chloride, and dissolved iron. The hypothesis is rejected at a slightly higher significance level (5 percent) for the paired t-test than the Wilcoxon signed ranks test (1 percent) for dissolved aluminum and dissolved manganese and at a slightly lower significance level (1 percent) for dissolved nickel and dissolved silver. Conclusions based on the paired

t-test are the same whether or not one deletes the sample pairs where USGS concentrations were less than the MDL for IEPA analyses but greater than the MDL for USGS analyses.

Relative Percentage Difference and Scatter

Only mean RPD's for dissolved sodium, alkalinity, and chloride were less than 10 percent, whereas those for 8 of the 15 constituents and properties in table 6 were greater than 50 percent. The scattergrams in figures 12–26 (at end of report) strongly agree with the RPD results. The scattergrams for dissolved sodium, alkalinity, and chloride (figs. 13, 15, and 16, respectively) show substantial agreement between IEPA and USGS concentrations. In contrast, the scattergrams for turbidity, ammonia, total phosphorus, dissolved aluminum, dissolved chromium, dissolved cobalt, dissolved iron, dissolved nickel, and dissolved silver (figs. 12, 17–19, 21–23, 25, and 26, respectively) show little agreement between IEPA and USGS concentrations and other

Table 6. Results of paired t-test and relative percentage difference analysis for U.S. Geological Survey and Illinois Environmental Protection Agency split samples of water from Illinois streams

[USGS, U.S. Geological Survey; IEPA, Illinois Environmental Protection Agency; MDL, method detection limit; N.A., not applicable; α , statistical significance level; RPD, relative percentage difference]

Constituent or property	Delete USGS values less than IEPA MDL	Number of sample pairs	Student's t^1	Bound on t statistic		Mean RPD (percent)
				$\alpha = 0.05$	$\alpha = 0.01$	
Turbidity	N.A.	160	-4.02	1.98	2.62	62.9
Sodium, dissolved	N.A.	189	3.19	1.98	2.62	7.97
Potassium, dissolved	N.A.	192	-5.14	1.98	2.62	20.6
Alkalinity	N.A.	142	-1.33	1.98	2.62	9.75
Chloride	N.A.	152	1.84	1.98	2.62	6.61
Ammonia	Yes	118	3.52	1.98	2.62	57.4
Ammonia	No	163	3.65	1.98	2.62	54.9
Phosphorus, total	N.A.	177	3.81	1.98	2.62	25.6
Aluminum, dissolved	Yes	80	2.52	1.99	2.65	112
Aluminum, dissolved	No	101	2.57	1.99	2.63	99.5
Barium, dissolved	N.A.	132	-6.31	1.98	2.62	11.7
Chromium, dissolved	Yes	32	6.91	2.02	2.74	124
Chromium, dissolved	No	47	6.03	2.01	2.69	96.3
Cobalt, dissolved	Yes	9	8.57	2.26	3.25	91.1
Cobalt, dissolved	No	10	5.82	2.23	3.17	83.9
Iron, dissolved	Yes	52	1.30	2.01	2.68	85.5
Iron, dissolved	No	126	1.83	1.98	2.62	83.9
Manganese, dissolved	Yes	123	2.40	1.98	2.62	33.8
Manganese, dissolved	No	118	2.39	1.98	2.62	33.4
Nickel, dissolved	Yes	48	2.93	2.01	2.69	96.1
Nickel, dissolved	No	111	3.65	1.98	2.62	65.4
Silver, dissolved	Yes	7	4.94	2.37	3.50	162
Silver, dissolved	No	22	3.32	2.07	2.82	77.6

¹Negative values indicate that concentrations measured in the U.S. Geological Survey laboratory tend to be higher than concentrations measured in the Illinois Environmental Protection Agency laboratory.

measurements. The lack of agreement is indicated by the high mean RPD's. Dissolved potassium and dissolved barium have fairly small mean RPD's, but the scattergrams for these constituents (figs. 14 and 20, respectively) show a clear tendency for the USGS concentrations to be greater than the IEPA concentrations. Finally, the scattergram for dissolved manganese (fig. 24) shows that these data follow the line of perfect agreement (1:1 line) throughout the range of the data but are considerably scattered about this line.

Consideration of Method and Interlaboratory Precision

Method precision, defined earlier in the discussion of the concurrent-sample program, also is of interest in examining results of the split-sample program. A second type of precision of interest to this study is agreement between laboratories in assessing split water-quality samples by use of identical analytical methods. This relative accuracy is known as interlaboratory precision. Concentrations of some constituents in the split samples analyzed in this study provide information on interlaboratory precision.

In the following subsections the differences between the USGS and IEPA measurements are compared to the method precision and interlaboratory precision for constituents and properties for which significant differences were identified by the Wilcoxon signed ranks test. The comparisons are only approximate because explicit relations for precision are not available for each constituent, the methods of laboratory analysis used by the USGS water-quality laboratory changed during the study period (1985–91) for some constituents, and no estimates are available for the precision of the IEPA laboratory methods (except indirectly where IEPA and USGS laboratory methods were the same).

Method Precision

Information on the precision of the methods used by the USGS water-quality laboratory during 1985–91 is given by Fishman and Friedman (1989) and Fishman (1993). For some constituents (for example, trace metals measured by the ICP method), the standard deviation resulting from method precision, S_p , is presented as a linear function of the measured concentration. For other constituents, available information on S_p did not conform to a mathematical relation between S_p and the constituent concentration; thus, S_p is tabulated in relation to various concentrations of the constituent. Despite

the approximate nature of the comparisons that follow, the differences in concentration for most constituents are much greater than can be attributed to laboratory precision alone.

Turbidity.—The USGS and IEPA laboratories both used the nephelometric method to measure turbidity. Fishman and Friedman (1989, p. 498) state that, according to data reported by the U.S. Environmental Protection Agency, the precision of data from a single laboratory expressed in terms of the percentage relative standard deviation was 2 percent for a sample whose mean turbidity was 0.26 NTU. The mean RPD for the turbidity data was 62.9 percent. Thus, even if the relative S_p was 10 times larger than the example above for samples with higher turbidities, the mean RPD is much larger than the uncertainty resulting from method precision.

Dissolved potassium.—The USGS and IEPA laboratories both used the atomic absorption, direct aspiration (AADA) method to measure dissolved potassium concentrations. S_p 's for samples whose concentrations are 1.02 mg/L or less are tabulated by Fishman and Friedman (1989, p. 394). Nearly all of the concentrations in the data pairs were between 1 and 8 mg/L. The relative S_p for the 1.02-mg/L sample was 4.6 percent. The mean RPD for the dissolved potassium data is 20.6 percent. Therefore, the mean RPD may be 4 to 5 times the relative standard deviation resulting from method precision.

Ammonia.—The IEPA laboratory used the automated phenate method to measure ammonia concentration, whereas the USGS laboratory used a combination of methods: the colorimetric, salicylate-hypochlorite, automated-segmented flow (CSHASF) method (modified in March 1988); and the low ionic-strength water, colorimetric, salicylate-hypochlorite, automated-segmented flow (LISW) method (beginning March 1986, modified May 1989). The CSHASF method is appropriate for samples whose concentrations are 0.01 to 1.5 mg/L, although higher concentrations may be diluted to this range. The average S_p for the earlier version of the CSHASF method was 0.035 mg/L for a range of 0.2 to 2.0 mg/L (Fishman and Friedman, 1989, p. 318). For the modified version of this method, S_p (in milligrams per liter) can be estimated by a regression equation developed from the data presented by Fishman (1993, p. 132):

$$S_p = 0.00816X + 0.00066. \quad (2)$$

Equation 2 has a coefficient of determination of 0.963 over the concentration (X) range of 0.06 to 1.23 mg/L.

The LISW method is appropriate for samples whose concentrations are 0.01 to 0.3 mg/L, although higher concentrations may be diluted to this range. Fishman (1993, p. 124) reports an S_p of approximately 0.005 mg/L for this method.

The earlier version of the CSHASF method was less precise than the modified version. A lower bound on the ratio between S_p and the concentration difference in USGS and IEPA measurements is obtained if S_p for the earlier version of the CSHASF method is used, whereas an upper bound is obtained if S_p for the modified version of the CSHASF method is used. The mean and the median of the ratios and the absolute values of the ratios are mean = -0.834 and median = -0.571 for the ratios with high S_p ; mean = 1.957 and median = 1.143 for the absolute value of the ratios with high S_p ; mean = -3.311 and median = -2.267 for the ratios with low S_p ; and mean = 7.765 and median = 4.535 for the absolute values of the ratios with low S_p .

Total phosphorus.—The IEPA laboratory used the manual persulfate digestion, automated ascorbic acid reduction method to measure the total phosphorus concentration. The USGS laboratory used the colorimetric, phosphomolybdate, automated-segmented flow method to measure the total phosphorus concentration. The USGS modified the method in May 1990 because inadequate dilution procedures caused the concentrations measured before May 1990 to be biased low (David Rickert, U.S. Geological Survey, Office of Water Quality, written commun., 1992). Because of this measurement bias in most of the USGS laboratory data for total phosphorus, the differences between USGS and IEPA data are not compared to measures of method precision in this report.

Dissolved aluminum.—The IEPA laboratory used the AADA method to measure dissolved aluminum concentration. Beginning in January 1986, the USGS laboratory used the atomic emission spectrometric, DC plasma (AESDCP) method to measure dissolved aluminum concentration. Before January 1986, a different method was used by the USGS laboratory, but the earlier data represent such a small part of the data collected in this study that the details and the precision of the earlier method can be omitted here. S_p values for several concentrations have been tabulated by Fishman (1993, p. 16). The following rules approximate the information provided by Fishman: for dissolved aluminum concentrations less than 50 $\mu\text{g/L}$, $S_p = 2.5 \mu\text{g/L}$; for dissolved aluminum concentrations from 50 to 200 $\mu\text{g/L}$, $S_p = 10 \mu\text{g/L}$; and for dissolved aluminum concentra-

tions greater than 200 $\mu\text{g/L}$, $S_p = 4$ percent of the concentration. By use of these rules, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_p are -34.0 and -12, respectively; the mean and the median of the absolute values of this ratio are 36.6 and 13, respectively.

Dissolved barium.—The USGS and IEPA laboratories both used the ICP method to measure dissolved barium concentrations. A linear-regression relation between S_p and dissolved barium concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_p are 3.60 and 2.75, respectively; the mean and the median of the absolute values of this ratio are 5.47 and 4.20, respectively.

Dissolved iron.—The USGS and IEPA laboratories both used the ICP method to measure dissolved iron concentrations. A linear-regression relation between S_p and dissolved iron concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_p are -208 and -87, respectively; the mean and the median of the absolute values of this ratio are 232 and 104, respectively.

Dissolved manganese.—The USGS and IEPA laboratories both used the ICP method to measure dissolved manganese concentrations. A linear-regression relation between S_p and dissolved manganese concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_p are -10.6 and -3.2, respectively; the mean and the median of the absolute values of this ratio are 22.1 and 9.7, respectively.

Dissolved nickel.—The IEPA laboratory used the AADA method to measure dissolved nickel concentrations. The USGS laboratory used the atomic absorption, spectrometric, chelation extraction (AASCE) method until April 1989 and the atomic absorption, spectrometric, graphite furnace (AASGF) method after April 1989 to measure dissolved nickel concentrations. (All nickel concentrations among the data pairs were less than or equal to 20 $\mu\text{g/L}$.) No information is available on S_p for the AASCE method. For the AASGF method, S_p (in micrograms per liter) can be estimated by a regression equation developed from the data presented by Fishman (1993, p. 116):

$$S_p = 0.0524X + 0.431. \quad (3)$$

The coefficient of determination for this equation is 0.904 over the concentration (X) range of 1.6 to 48.1 $\mu\text{g/L}$. If this equation is used to estimate S_p for all the data, a rough approximation of the ratio of the difference between USGS and IEPA concentrations and S_p is obtained. The mean and the median of this ratio are -3.29 and -0.93 , respectively; the mean and the median of the absolute values of this ratio are 5.04 and 3.10, respectively.

Dissolved sodium.—The USGS and IEPA laboratories both used the ICP method to measure dissolved sodium concentrations. A linear-regression relation between S_p and dissolved sodium concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_p are 1.46 and 1.31, respectively; the mean and the median of the absolute values of this ratio are 4.32 and 2.78, respectively.

Dissolved chromium.—The IEPA laboratory used the AADA method to measure dissolved chromium concentrations. The USGS laboratory used the AASCE method until November 1987 and the AESDCP method after November 1987 to measure dissolved chromium concentrations. (All chromium concentrations among the data pairs were less than or equal to 10 $\mu\text{g/L}$.) No information is available on S_p for the AASCE method. S_p 's for several dissolved chromium concentrations measured by the AESDCP method have been tabulated by Fishman (1993, p. 62). For concentrations in the range of the data in this study, S_p equals approximately 0.7 $\mu\text{g/L}$. By use of this S_p value, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_p are -4.26 and -4.64 , respectively; the mean and the median of the absolute values of this ratio are 4.98 and 5.73, respectively.

Dissolved cobalt.—The USGS and IEPA laboratories both used the ICP method to measure dissolved cobalt concentrations. A linear-regression relation between S_p and dissolved cobalt concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA measured concentrations and S_p are -6.94 and -6.22 , respectively; the mean and the median of the absolute values of this ratio are 7.11 and 6.22, respectively.

Dissolved silver.—The IEPA laboratory used the AADA method to measure dissolved silver concentrations. The USGS laboratory used the AASCE method until April 1989 and the AASGF method after April 1989 to measure dissolved silver concentrations. No information is available on S_p for the AASCE method. The information provided by Fishman (1993, p. 208) on S_p for the AASGF method is too inconsistent over a small range of concentrations to provide a useful and meaningful comparison of the differences between the USGS and IEPA concentrations.

Alkalinity.—The IEPA laboratory used the automated methyl orange method to measure alkalinity. The USGS laboratory used the low ionic-strength water, electrometric titration method (automated in January 1986) to measure alkalinity. No information on S_p is available for either method.

Chloride.—The USGS and IEPA laboratories both used the colorimetric, ferric thiocyanate, automated-segmented flow method to measure chloride concentrations. No information is available on S_p for this method.

Interlaboratory Precision

The meager amount of information available on the interlaboratory precision of the methods used by the USGS water-quality laboratory during 1985–91 is given by Fishman and Friedman (1989) and Fishman (1993). For some constituents, the standard deviation resulting from interlaboratory precision, S_T , is presented as a linear function of the measured concentration. For other constituents, the available information on S_T did not conform to a mathematical relation between S_T and the constituent concentration, and S_T is tabulated in relation to various constituent concentrations. For turbidity, ammonia, total phosphorus, and dissolved aluminum, no information is available on the interlaboratory precision; thus, measurements of turbidity and these three constituents are not discussed in detail in the paragraphs that follow.

For constituents measured by the ICP method, Fishman and Friedman (1989, p. 522) note that the interlaboratory precision data were obtained from the USGS SRSAEP (described by Long and Farrar, 1992). They further note that the ICP method may not have been used by all laboratories; thus, the S_T obtained from the regression equations presented by Fishman and Friedman (1989, p. 522) may represent

a more general interlaboratory precision for the constituent under consideration.

An additional comparison of the interlaboratory precision is given in table 7. In this table, the average rating of the USGS and IEPA laboratories from the SRSAEP (described by Long and Farrar, 1992) is given for 1985–91 for several constituents and alkalinity in the split samples. Turbidity, dissolved phosphorus, and dissolved chromium are not listed in table 7 because they were not evaluated in the SRSAEP, whereas ammonia is not listed because the IEPA laboratory did not test for ammonia. Both laboratories were rated good to excellent for all constituents except dissolved potassium, dissolved cadmium, dissolved cobalt, and dissolved silver (for which the IEPA laboratory was rated satisfactory to good) and dissolved beryllium (for which the USGS laboratory was rated satisfactory to good). Therefore, the relatively small ratios of the difference between USGS and IEPA concentrations and S_T reported below are typical of the interlaboratory performance of laboratories that are rated good to excellent.

Dissolved potassium.—The USGS and IEPA laboratories both used the AADA method to measure dissolved potassium concentrations. A linear-regression equation between S_T and concentration for samples having concentrations between 0.09 and 26.1 mg/L is given by Fishman and Friedman (1989, p. 394). Nearly all of the dissolved potassium concentrations in this study were between 1 and 8 mg/L. The mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are 1.22 and 0.94, respectively; the mean and the median of the absolute value of these ratios are 1.85 and 1.22, respectively.

Dissolved barium.—The USGS and IEPA laboratories both used the ICP method to measure dissolved barium concentrations. A linear-regression relation between S_T and dissolved barium concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are 0.82 and 0.65, respectively; the mean and the median of the absolute values of this ratio are 1.29 and 1.04, respectively.

Dissolved iron.—The USGS and IEPA laboratories both used the ICP method to measure dissolved iron concentrations. A linear-regression relation between S_T and dissolved iron concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are -0.98 and -0.66 , respec-

Table 7. Average rating of U.S. Geological Survey and Illinois Environmental Protection Agency laboratories determined by the U.S. Geological Survey Standard Reference Sample Analytical-Evaluation Program, 1985–91 [USGS, U.S. Geological Survey; IEPA, Illinois Environmental Protection Agency; --, constituent not analyzed for by IEPA laboratory]

Constituent or property	USGS laboratory		IEPA laboratory	
	Number of samples	Average rating ¹	Number of samples	Average rating ¹
Calcium, dissolved	2	3	29	3
	9	.72		.41
Magnesium, dissolved	2	3	29	3
	9	.76		.62
Sodium, dissolved	2	3	29	3
	9	.60		.41
Potassium, dissolved	2	3	28	2
	6	.65		.71
Alkalinity	1	3	16	3
	4	.57		.06
Sulfate	1	3	16	3
	5	.53		.06
Chloride	1	3	17	3
	5	.47		.35
Nitrate	1	3	6	3
	7	.82		.33
Nitrite	1	3	--	-
	4	.29		-
Phosphorus, total	3	3	14	3
	0	.30		.57
Aluminum, dissolved	1	3	11	3
	3	.92		.36
Barium, dissolved	1	3	14	3
	2	.75		.36
Beryllium, dissolved	1	2	10	3
	0	.60		.70
Cadmium, dissolved	1	3	13	2
	3	.61		.92
Cobalt, dissolved	1	3	10	2
	3	.15		.50

tively; the mean and the median of the absolute values of this ratio are 2.65 and 0.79, respectively.

Dissolved manganese.—The USGS and IEPA laboratories both used the ICP method to measure dissolved manganese concentrations. A linear-regression relation between S_T and dissolved manganese concentration is given by Fishman and Friedman

(1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are -0.26 and -0.087 , respectively; the mean and the median of the absolute values of this ratio are 0.70 and 0.32 , respectively.

Dissolved nickel.—The IEPA laboratory used the AADA method to measure dissolved nickel concentrations. The USGS laboratory used the AASCE method until April 1989 and the AASGF method after April 1989 to measure dissolved nickel concentrations. (All nickel concentrations in the data pairs were less than or equal to $20 \mu\text{g/L}$.) No information is available on S_T for the AASGF method. Fishman and Friedman (1989, p. 300) report that the average value of S_T for the AASCE method was $4.3 \mu\text{g/L}$ independent of concentration in the range 3.8 to $23.2 \mu\text{g/L}$. By use of this value for S_T , the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are -0.34 and -0.12 , respectively; the mean and the median of the absolute values of this ratio are 1.01 and 0.35 , respectively.

Dissolved sodium.—The USGS and IEPA laboratories both used the ICP method to measure dissolved sodium concentrations. A linear-regression relation between S_T and dissolved sodium concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are 0.46 and 0.40 , respectively; the mean and the median of the absolute values of this ratio are 1.35 and 0.90 , respectively.

Dissolved chromium.—The IEPA laboratory used the AADA method to measure dissolved chromium concentrations. The USGS laboratory used the AASCE method until November 1987 and the AESDCP method after November 1987 to measure dissolved chromium concentrations. (All chromium concentrations in the data pairs were less than or equal to $10 \mu\text{g/L}$.) No information is available on S_T for the AESDCP method. Fishman and Friedman (1989, p. 165) report that the average value of S_T for the AASCE method was $13.2 \mu\text{g/L}$ independent of concentration in the range 5.8 to $47.8 \mu\text{g/L}$. By use of this value for S_T , the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are -0.25 and -0.24 , respectively; the mean and the median of the absolute values of this ratio are 0.26 and 0.30 , respectively.

Dissolved cobalt.—The USGS and IEPA laboratories both used the ICP method to measure dissolved cobalt concentrations. A linear-regression relation

between S_T and dissolved cobalt concentration is given by Fishman and Friedman (1989, p. 522). By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are -1.18 and -1.06 , respectively; the mean and the median of the absolute values of this ratio are 1.21 and 1.06 , respectively.

Dissolved silver.—The IEPA laboratory used the AADA method to measure dissolved silver concentrations. The USGS laboratory used the AASCE method until April 1989 and the AASGF method after April 1989 to measure dissolved silver concentrations. No information is available on S_T for the AASGF method. A linear-regression equation between S_T and dissolved silver concentration for the AASCE method is given by Fishman and Friedman (1989, p. 424). This equation is valid for dissolved silver concentrations between 1.5 and $13.6 \mu\text{g/L}$, whereas nearly all of the USGS concentrations were less than $1.5 \mu\text{g/L}$. Therefore, no ratios could be computed for dissolved silver.

Alkalinity.—The IEPA laboratory used the automated methyl orange method to measure alkalinity. The USGS laboratory used the low ionic-strength water, electrometric titration method (automated in January 1986) to measure alkalinity. Fishman and Friedman (1989, p. 58) report that the average value of S_T for the electrometric titration method was 6.7 mg/L independent of concentration in the range 18.4 to 303 mg/L . By use of this value for S_T , the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are 0.27 and 0.15 , respectively; the mean and the median of the absolute values of this ratio are 1.35 and 0.75 , respectively.

Chloride.—The USGS and IEPA laboratories both used the colorimetric, ferric thiocyanate, automated-segmented flow method to measure chloride concentrations. The American Society for Testing and Materials (1984) reports that S_T equals 0.054 times the measured chloride concentration for this method. By use of this relation, the mean and the median of the ratio of the difference between the USGS and IEPA concentrations and S_T are -0.48 and -0.35 , respectively; the mean and the median of the absolute values of this ratio are 1.33 and 0.81 , respectively.

Significance of Differences

The results of the statistical tests and other analyses of the split water-quality samples are summarized in table 8. Differences were clearly significant between USGS and IEPA laboratory determinations of turbidity, dissolved potassium, ammonia, total phosphorus, dissolved aluminum, dissolved barium, dissolved iron, dissolved manganese, and dissolved nickel as indicated by the significance level for the statistical tests (table 8), high mean RPD's, high data scatter (figs. 12, 14, 17–20, and 23–25), and high mean and median ratios of differences between USGS and IEPA determinations to S_p . The result for total phosphorus was expected because of known problems in USGS laboratory analyses for phosphorus that were corrected in 1990 and 1991 (David Rickert, U.S. Geological Survey, Office of Water Quality, written commun., 1992). Differences in concentrations of dissolved sodium were statistically significant (rejection at low α values in table 4) but not practically important (low mean RPD, low scatter in fig. 13, and low mean and median ratios to S_p). For alkalinity and chloride, only the Wilcoxon signed ranks test indicated a statistically significant difference in the samples; thus, the differences were probably not important from a practical point of view. Differences in concentrations of dissolved chromium, dissolved cobalt, and dissolved silver may have been significant between the samples, but the number of sample pairs

available for comparison of these water-quality constituents was too small to allow any conclusions.

For all constituents for which data on interlaboratory precision are available, the mean and the median ratios of the differences between USGS and IEPA measured concentrations and S_T were less than 1.25 and less than 0.5 for 6 of the 10 constituents examined. Therefore, consideration of interlaboratory precision indicates that although the differences between USGS and IEPA measurements may have been statistically significant and (or) practically important, these differences are not unusual for interlaboratory comparisons. Implications of the findings of this study are that (1) water-quality regulators, planners, and engineers should be careful when using water-quality data to make decisions on compliance with regulations, methods to improve water quality, water-quality-model development, or other water-quality issues, and (2) data from different laboratories should not be mixed in statistical analyses, such as trend analysis.

Table 8. Summary of statistical-test results and other analyses of U.S. Geological Survey and Illinois Environmental Protection Agency split samples of water from Illinois streams
[RPD, relative percentage difference; MDL, method detection limit; --, not determined]

Constituent or property	Significance level for given test		Mean RPD (percent)	Amount of scatter about 1:1 line	Sample pairs where both concentrations exceeded greatest MDL
	Wilcoxon signed ranks	Paired t-test			
Turbidity	0.01	0.01	62.9	Hi	160
Sodium, dissolved	.01	.01	7.97	gh	189
Potassium, dissolved	.01	.01	20.6	w	192
Alkalinity	.05	--	9.75	gh	142
Chloride	.05	--	6.61	Lo	152
Ammonia	.01	.01	57.4	w	118
Phospho- rus, total	.01	.01	25.6	gh	177
				gh	

SUMMARY AND CONCLUSIONS

This report presents results of statistical tests and other comparisons of two sets of water-quality data collected and analyzed during 1985–91:

(1) samples collected concurrently by the USGS and IEPA and (2) split samples analyzed by USGS and IEPA water-quality laboratories. The comparisons of the concurrent samples involved 63 water-quality constituents and properties, whereas comparisons of the split samples involved 27 constituents and properties.

For concurrent samples, the Wilcoxon signed ranks test indicated significant differences between results of analyses for USGS and IEPA samples for 10 of the 63 (16 percent) constituents and properties. These 10 were further examined by use of the paired t-test, mean relative percentage difference, and scattergrams to determine if the differences were important from a practical point of view. For 7 of the 10, the differences in results of analyses between the concurrent samples were also compared to available information on the precision of the laboratory or field method. Mean relative percentage differences greater than 10 percent, high scatter of the data relative to the line of perfect agreement (1:1) between the IEPA and USGS constituent concentrations, or large ratios between the differences and the standard deviation resulting from method precision indicate that differences in the concentrations are large enough to concern water-quality engineers and planners. Conclusions based on the various comparisons follow:

1. Differences between USGS and IEPA measurements of pH and of ammonia concentration were significant.
2. Differences between USGS and IEPA measurements of dissolved oxygen and dissolved barium concentrations were statistically significant but not large enough to concern water-quality engineers and planners.
3. Only the Wilcoxon signed ranks test indicated significant differences in dissolved magnesium, dissolved sodium, and dissolved calcium between USGS and IEPA samples. All other comparisons indicate that differences were acceptably small for these constituents.
4. Significance of differences in results of analyses for the USGS and IEPA samples for total lead, dissolved zinc, and total cyanide could not be

determined because the number of data pairs for these constituents was too small to draw conclusions.

Therefore, USGS and IEPA field personnel seem to have collected and handled water samples in a comparable and reliable manner.

For split samples, the Wilcoxon signed ranks test indicated significant differences between results of analyses of the USGS and IEPA samples for 15 of the 27 (56 percent) constituents and properties. These 15 were further examined by use of the paired t-test, mean relative percentage difference, and scattergrams to determine if the differences were large enough to concern water-quality engineers and planners. The differences in results of analyses for the split samples were also compared to available information on the precision of the laboratory method and interlaboratory precision for a given constituent or property for 11 of 15 and 10 of 15 constituents and properties, respectively. Conclusions based on the various comparisons follow:

1. Differences between USGS and IEPA measurements of turbidity were significant; differences between USGS and IEPA measurements of dissolved potassium, ammonia, total phosphorus, dissolved aluminum, dissolved barium, dissolved iron, dissolved magnesium, and dissolved nickel concentrations were also significant.
2. Differences between USGS and IEPA measurements of dissolved sodium concentrations were statistically significant but not large enough to concern water-quality engineers and planners.
3. Only the Wilcoxon signed ranks test indicated significant differences for alkalinity and chloride between USGS and IEPA samples. All other comparisons indicate that differences were acceptably small.
4. Significance of differences between results of the USGS and IEPA analyses for dissolved chromium, dissolved cobalt, and dissolved silver could not be determined because the number of data pairs for these constituents was too small to draw conclusions.

This study demonstrates the difficulty in obtaining consistent measurements of selected water-quality constituents or properties. The USGS and IEPA

laboratories are generally rated good to excellent in the twice-yearly USGS Standard Reference Sample Analytical Evaluation Program for quality assurance, yet the differences in their measurements of some constituents and properties are statistically significant and large enough to concern water-quality engineers and planners. In a comparison of analyses of the split samples sent to the two laboratories, it was shown that the differences in measured concentrations for 9 of 27 water-quality constituents were large in any of five (Wilcoxon signed ranks test, paired t-test, mean relative percentage difference, scattergrams, and comparison to the standard deviation resulting from method precision) measures of the difference. These differences were not unusually large, however, with respect to available data on interlaboratory precision. Implications of the findings of this study are that (1) water-quality regulators, planners, and engineers need to be careful when using water-quality data to make decisions on compliance with regulations, methods to improve water quality, water-quality-model development, or other water-quality issues, and (2) data from different laboratories should not be mixed in statistical analyses, such as trend analysis.

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FIGURES 2-26

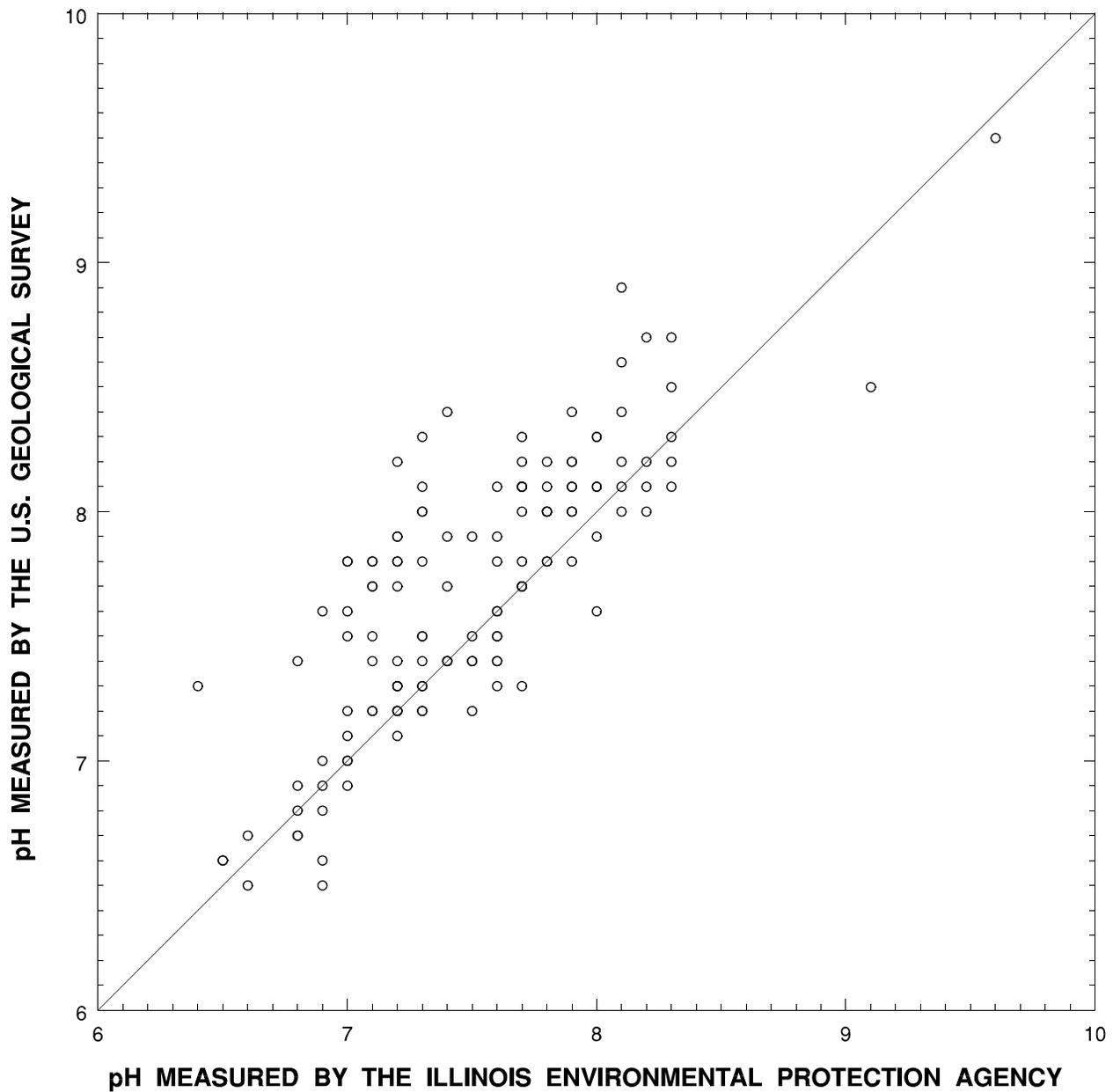


Figure 2. pH of paired concurrent samples of water from Illinois streams.

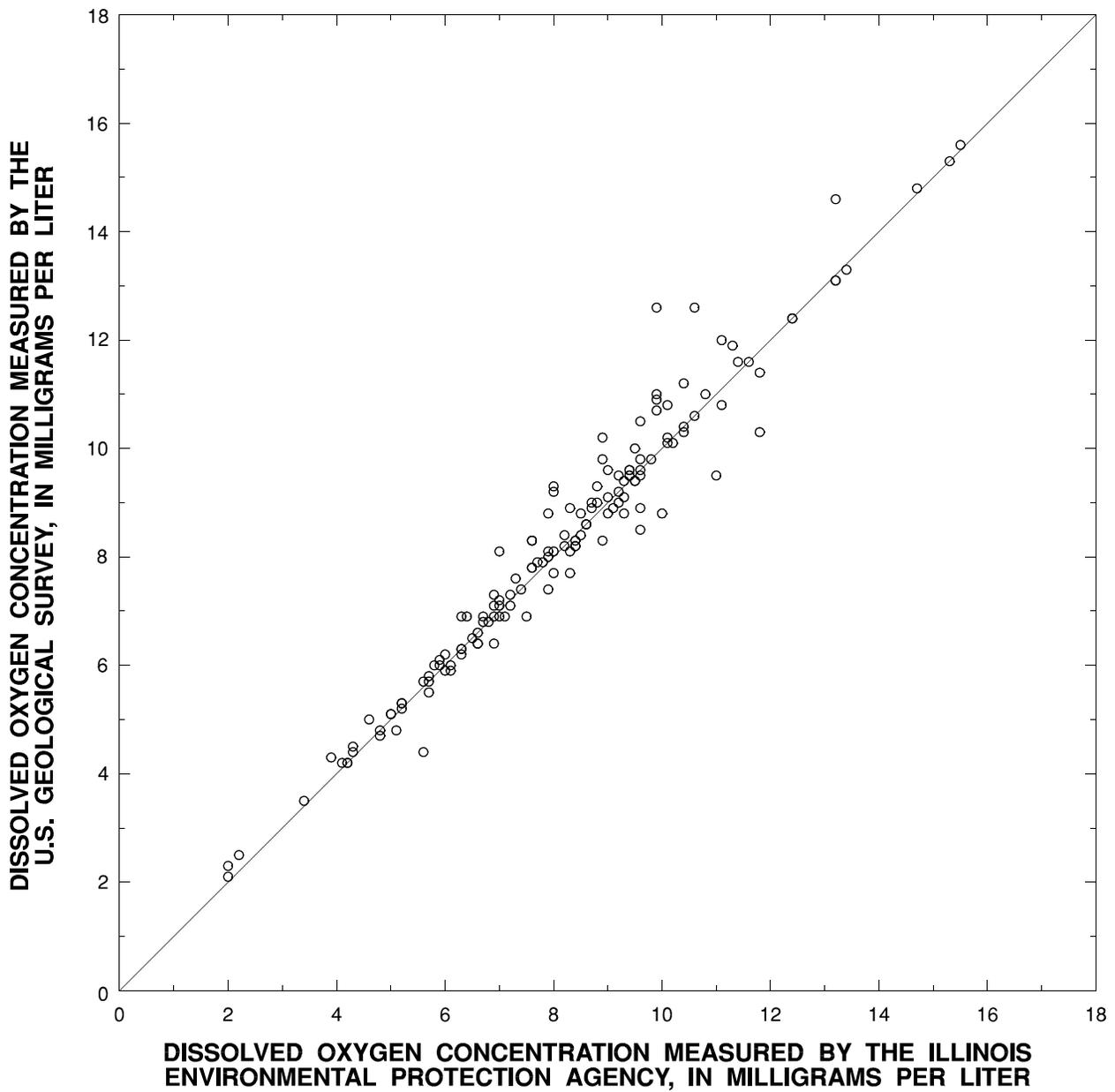


Figure 3. Dissolved oxygen concentration in paired concurrent samples of water from Illinois streams.

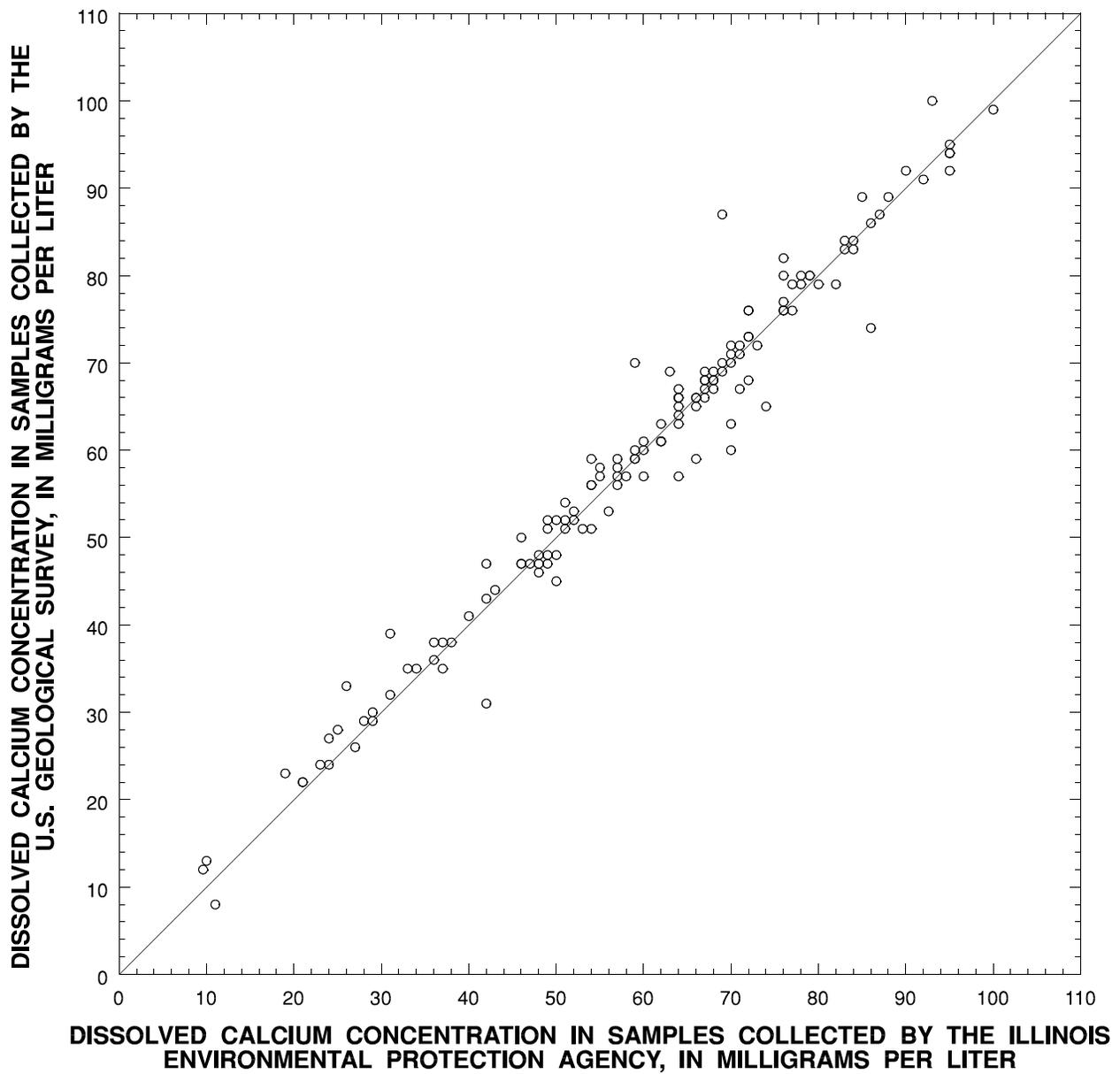


Figure 4. Dissolved calcium concentration in paired concurrent samples of water from Illinois streams.

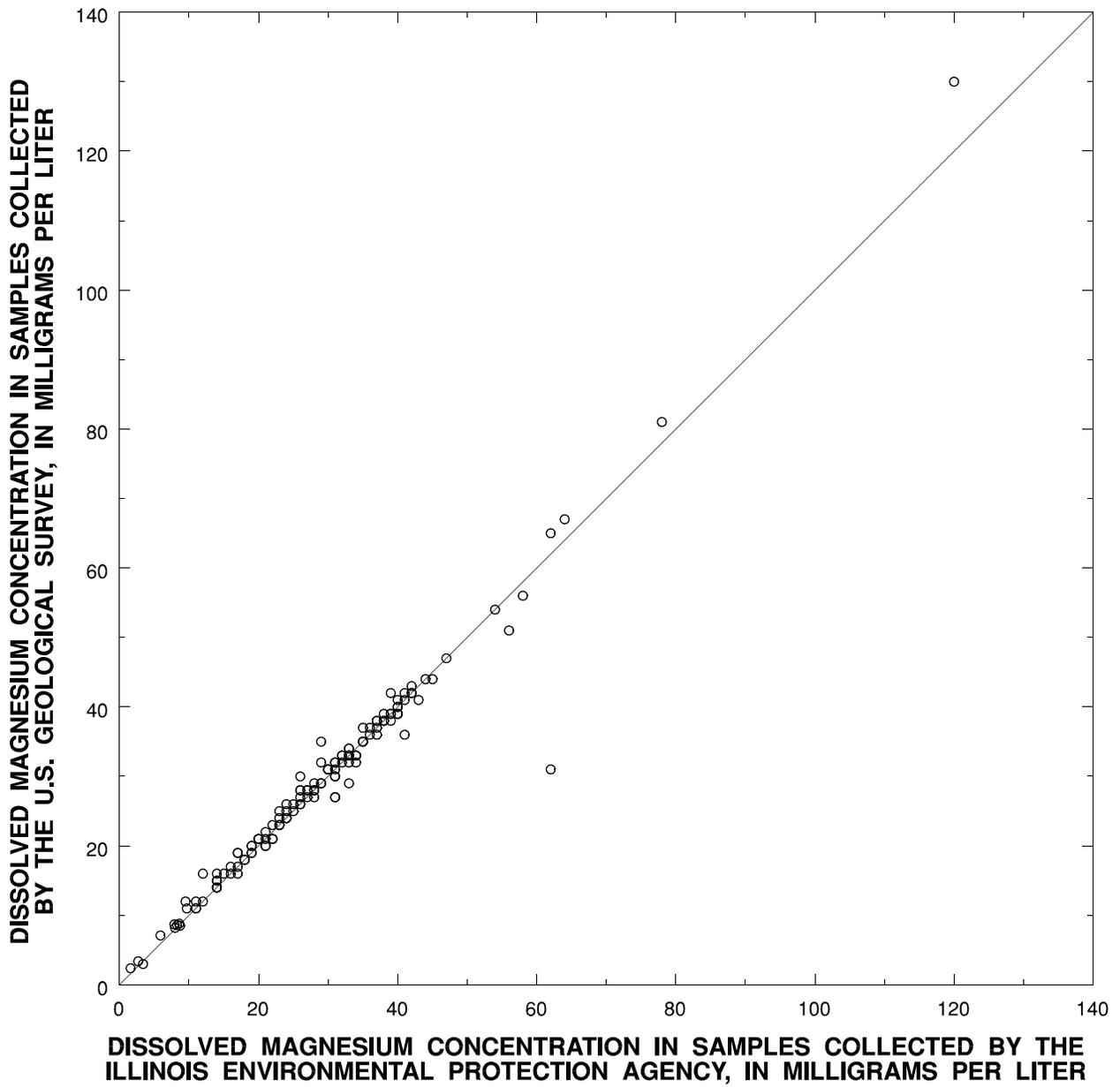


Figure 5. Dissolved magnesium concentration in paired concurrent samples of water from Illinois streams.

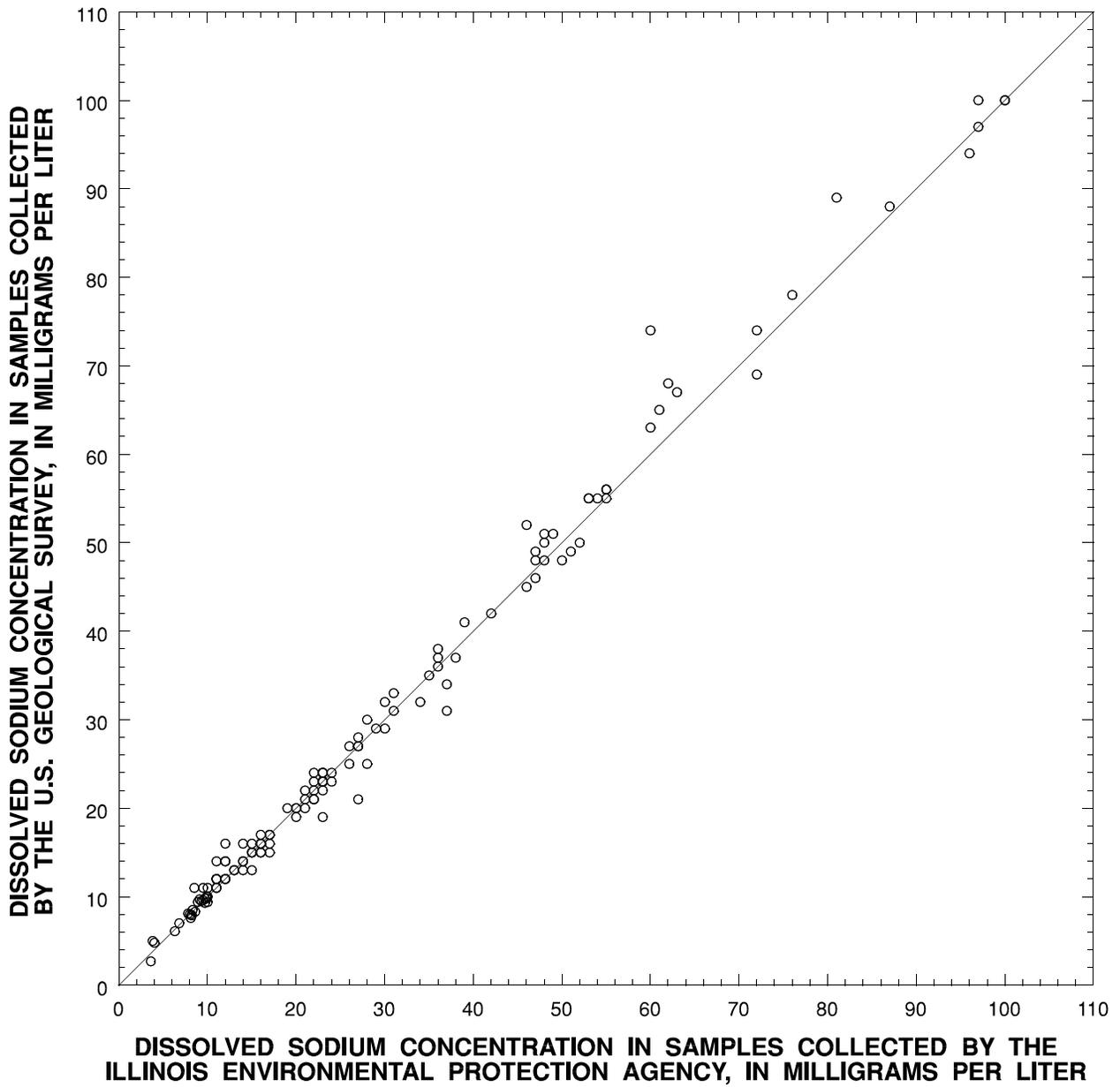


Figure 6. Dissolved sodium concentration in paired concurrent samples of water from Illinois streams.

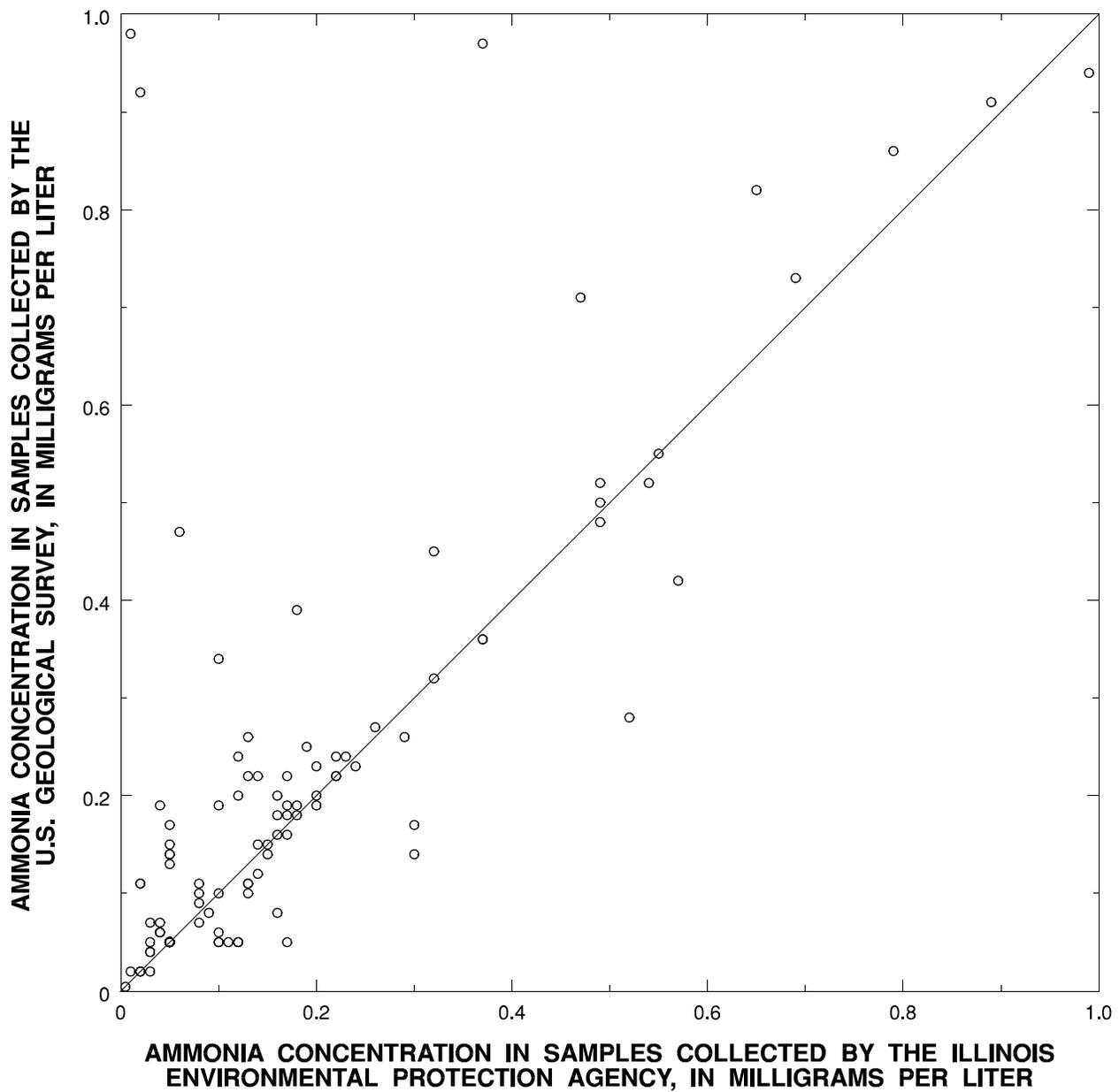


Figure 7. Ammonia concentration in paired concurrent samples of water from Illinois streams.

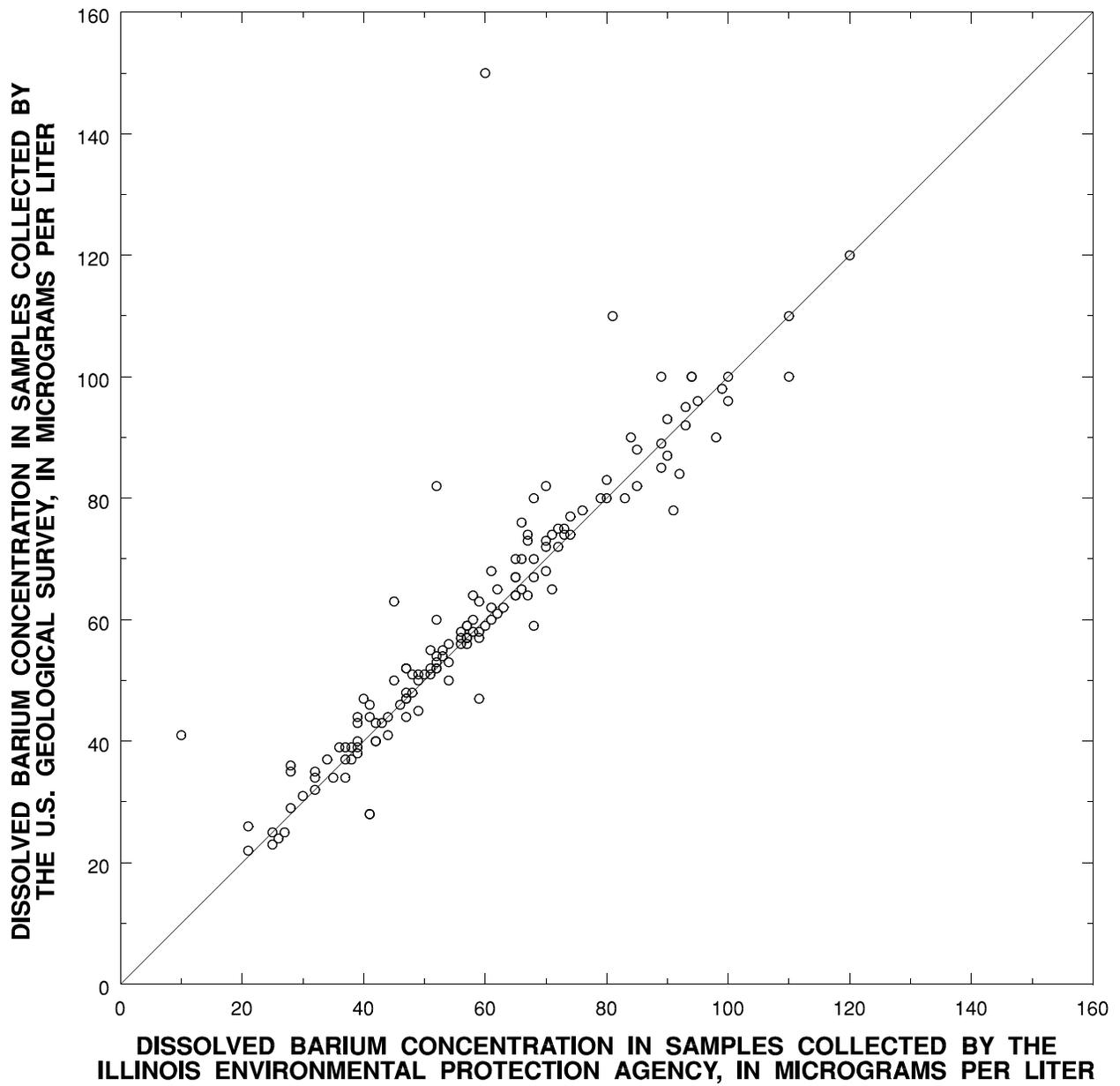


Figure 8. Dissolved barium concentration in paired concurrent samples of water from Illinois streams.

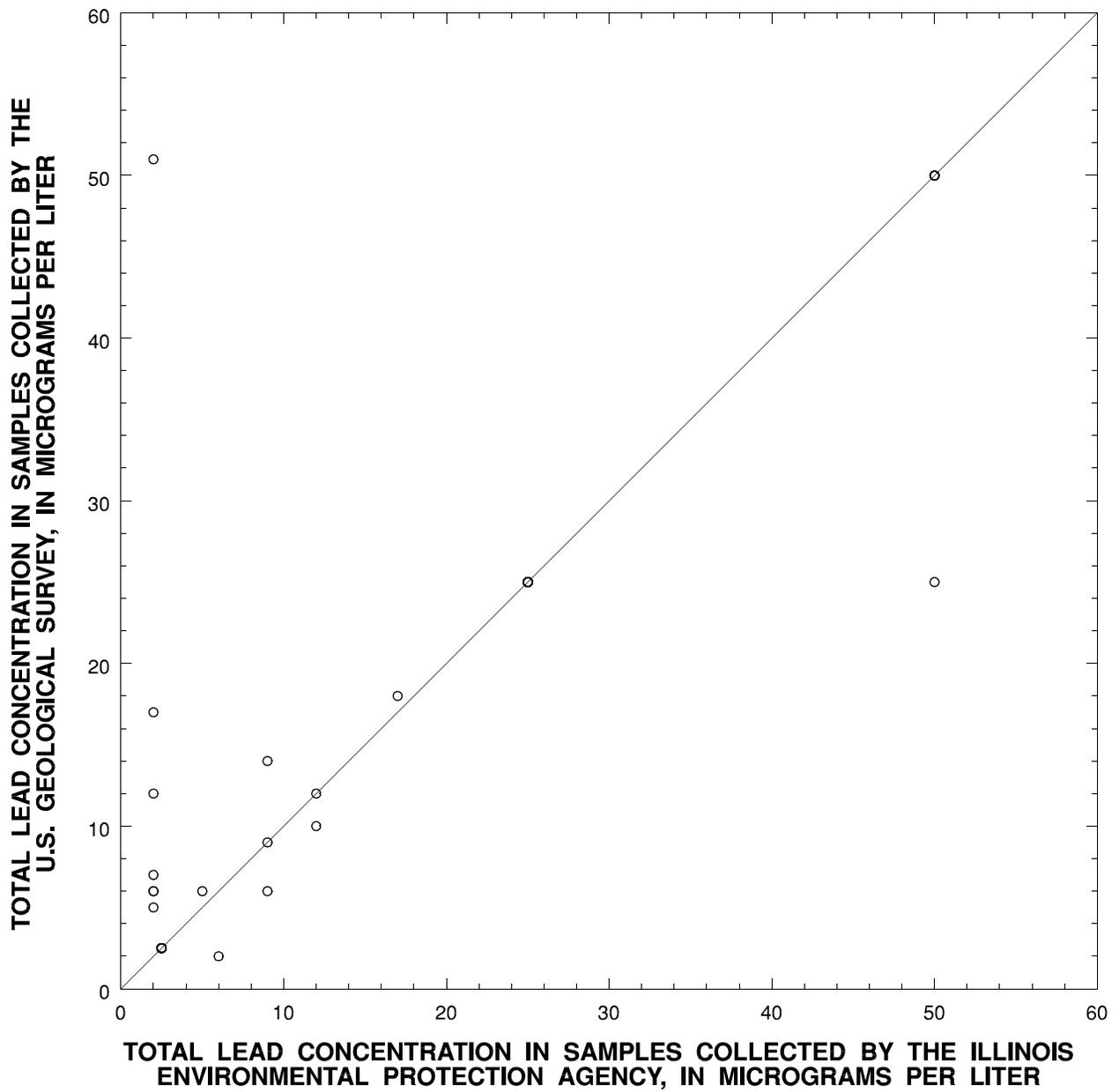


Figure 9. Total lead concentration in paired concurrent samples of water from Illinois streams.

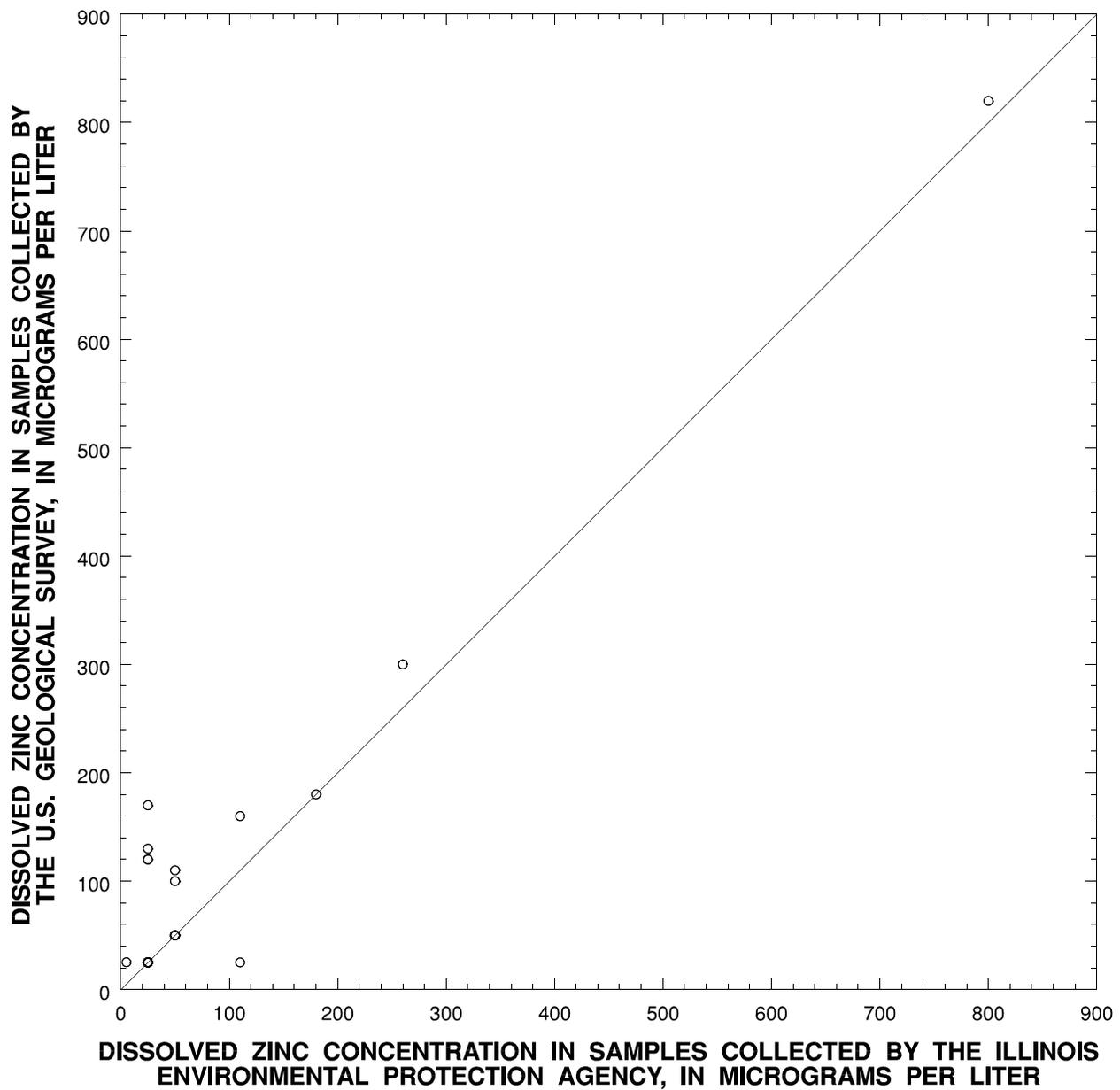
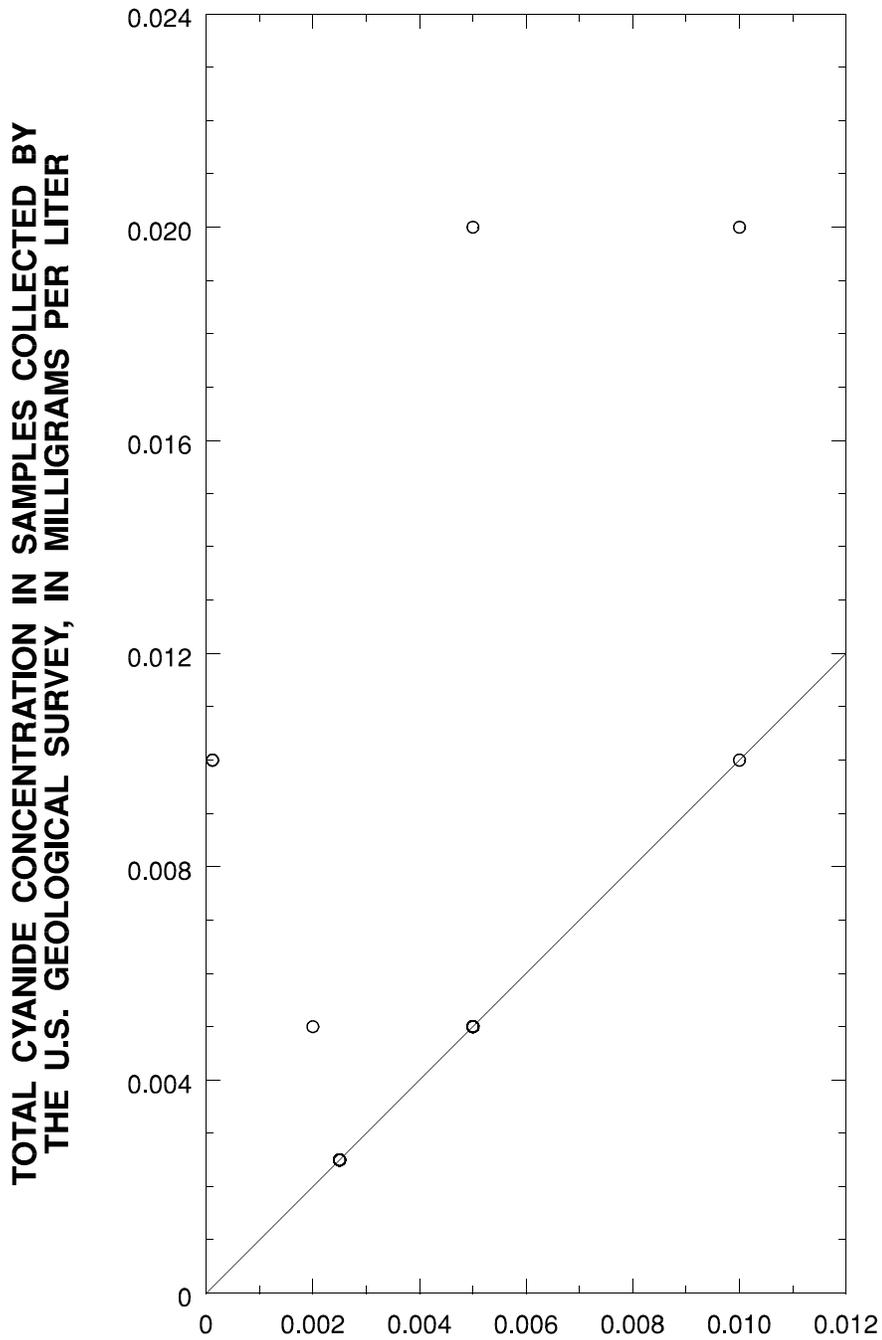


Figure 10. Dissolved zinc concentration in paired concurrent samples of water from Illinois streams.



TOTAL CYANIDE CONCENTRATION IN SAMPLES COLLECTED BY THE ILLINOIS ENVIRONMENTAL PROTECTION AGENCY, IN MILLIGRAMS PER LITER

Figure 11. Total cyanide concentration in paired concurrent samples of water from Illinois streams.

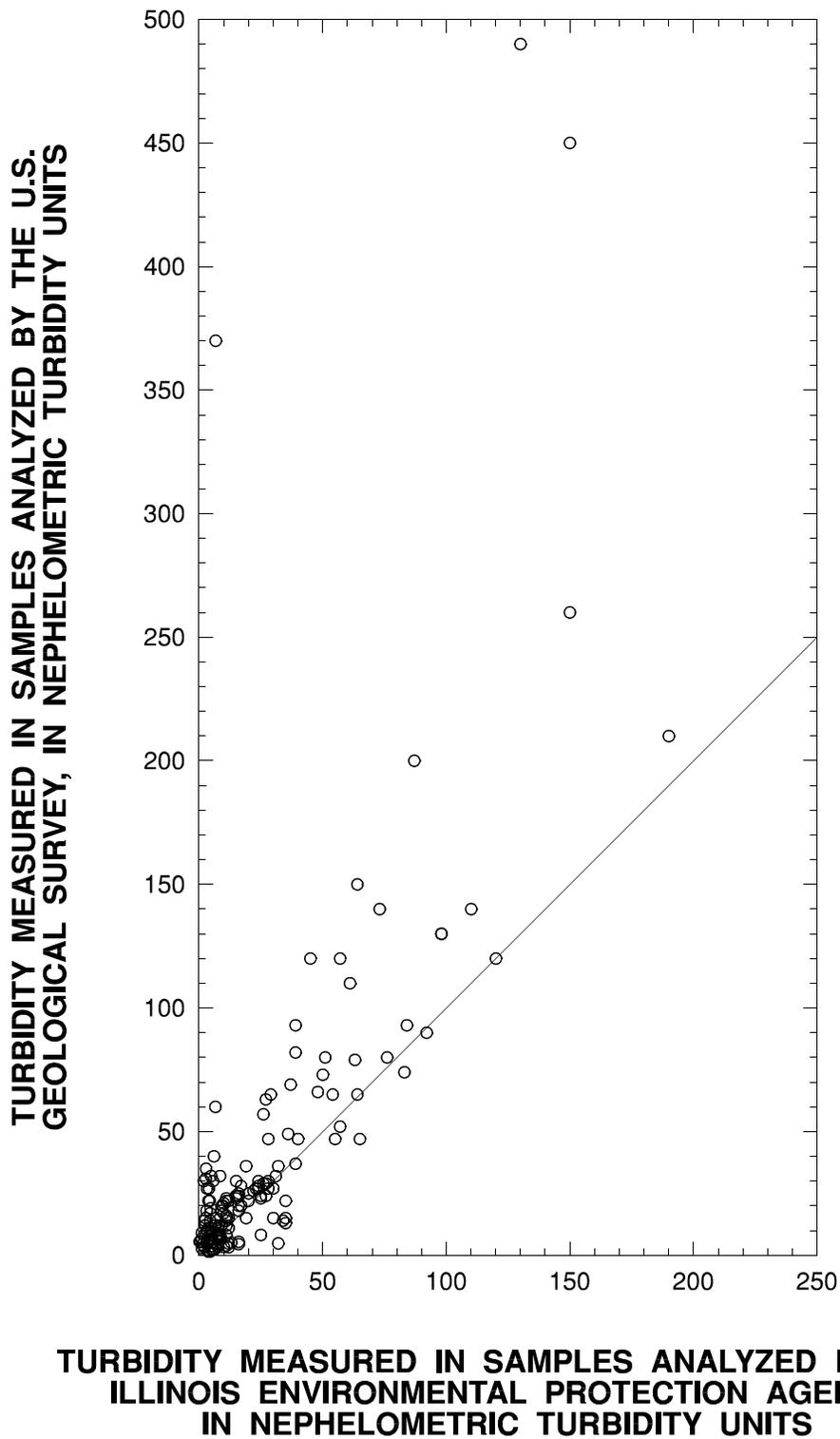


Figure 12. Turbidity in paired split samples of water from Illinois streams.

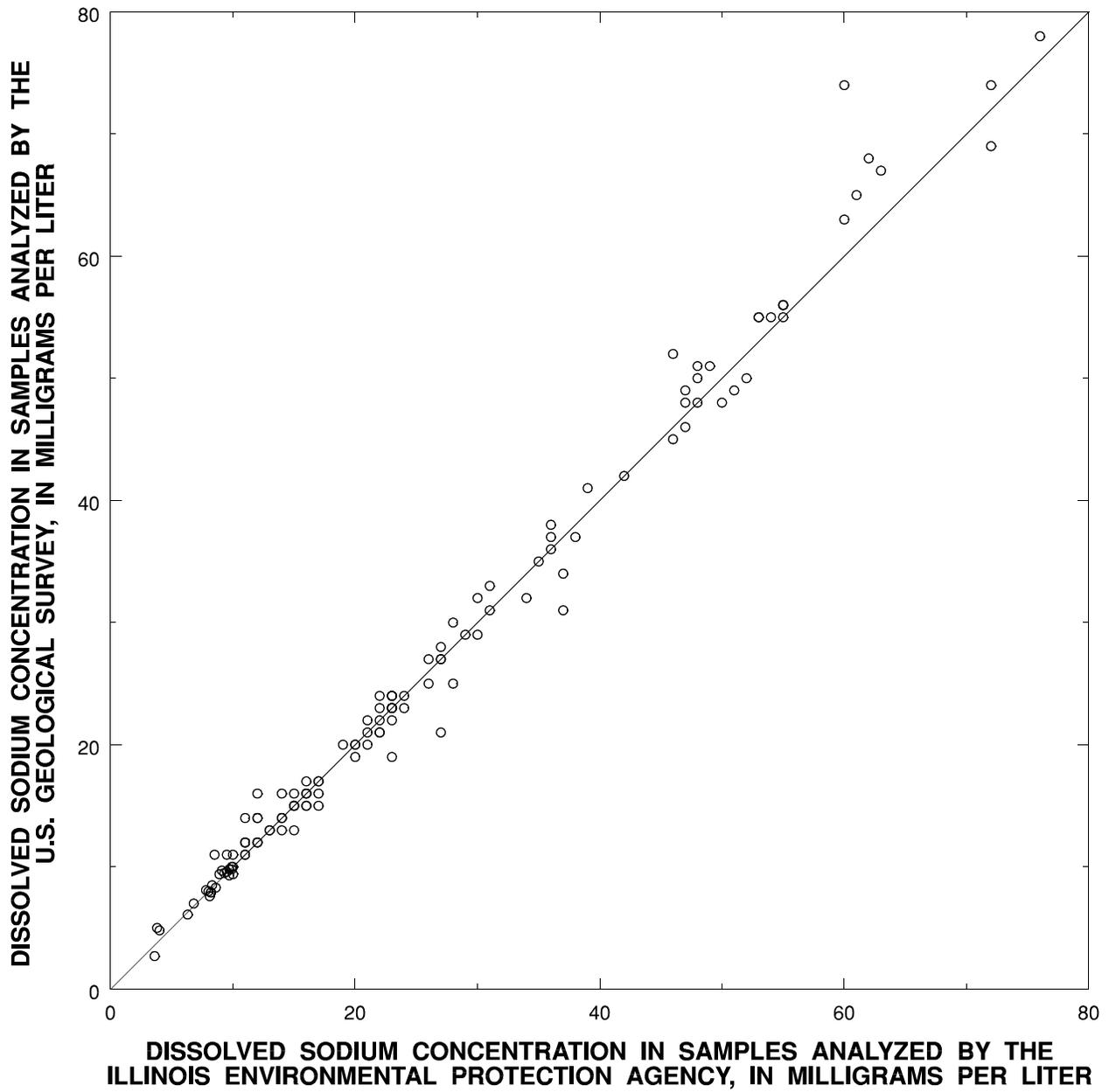


Figure 13. Dissolved sodium concentration in paired split samples of water from Illinois streams.

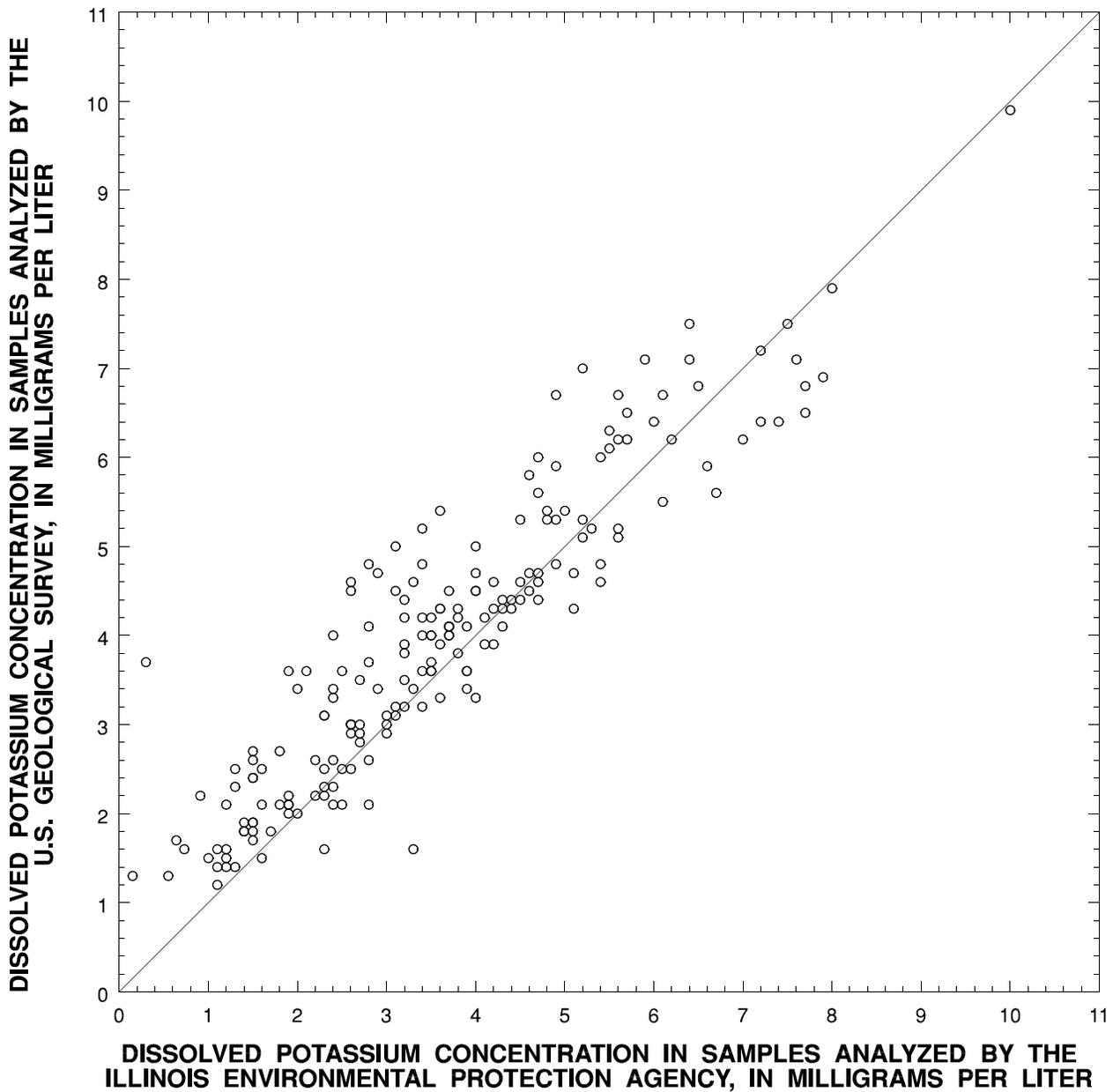


Figure 14. Dissolved potassium concentration in paired split samples of water from Illinois streams.

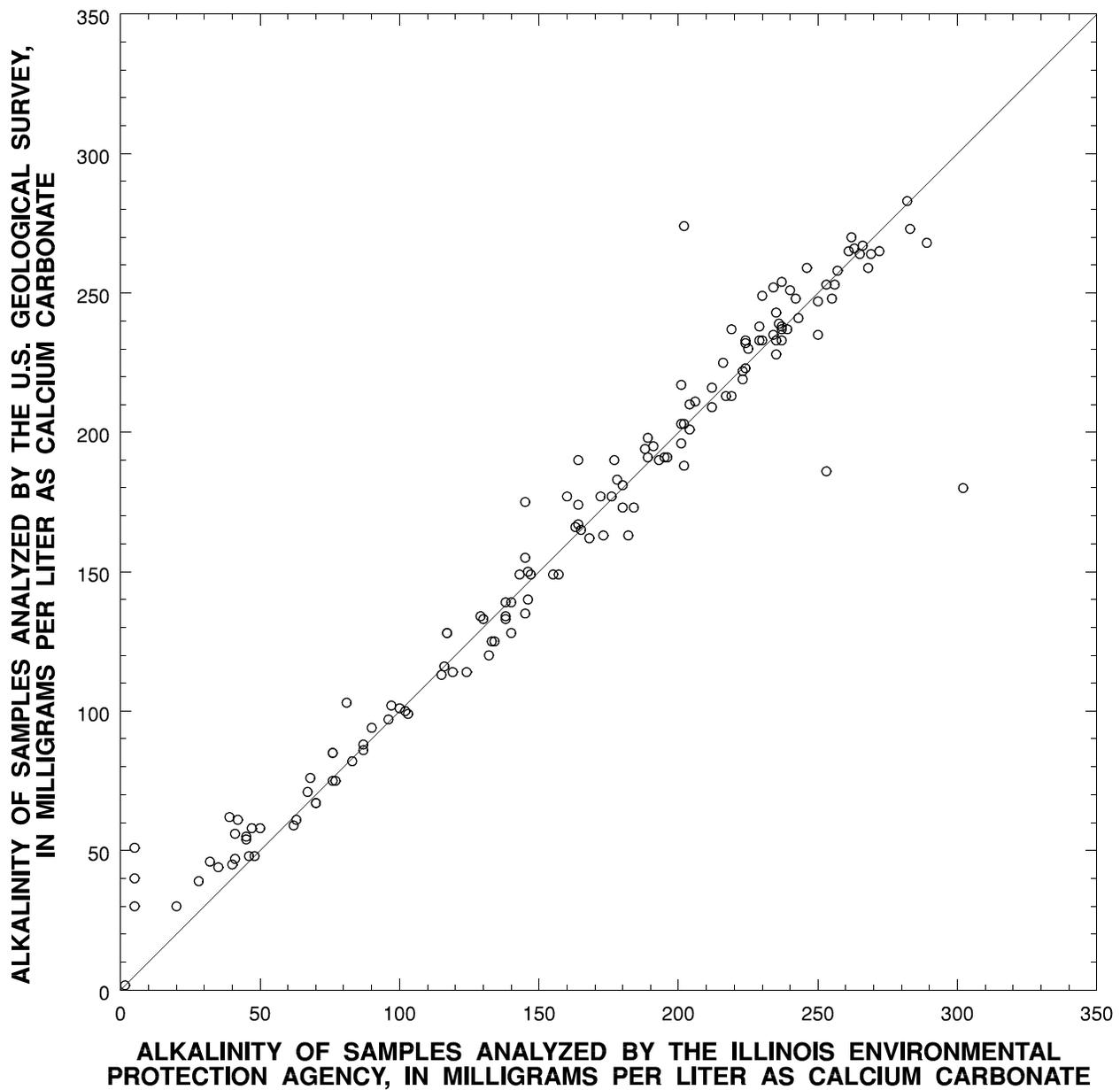


Figure 15. Alkalinity of paired split samples of water from Illinois streams.

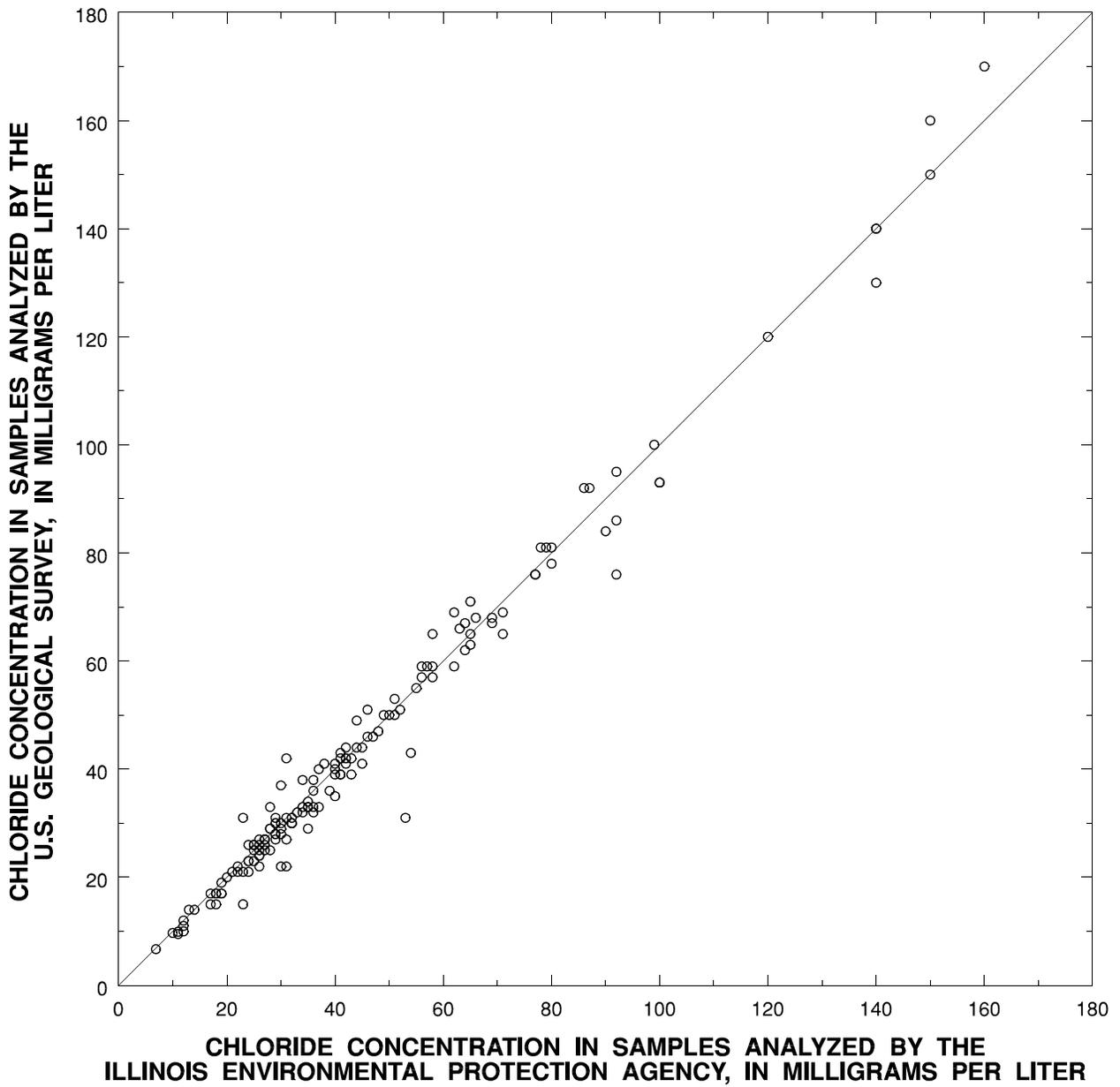


Figure 16. Chloride concentration in paired split samples of water from Illinois streams.

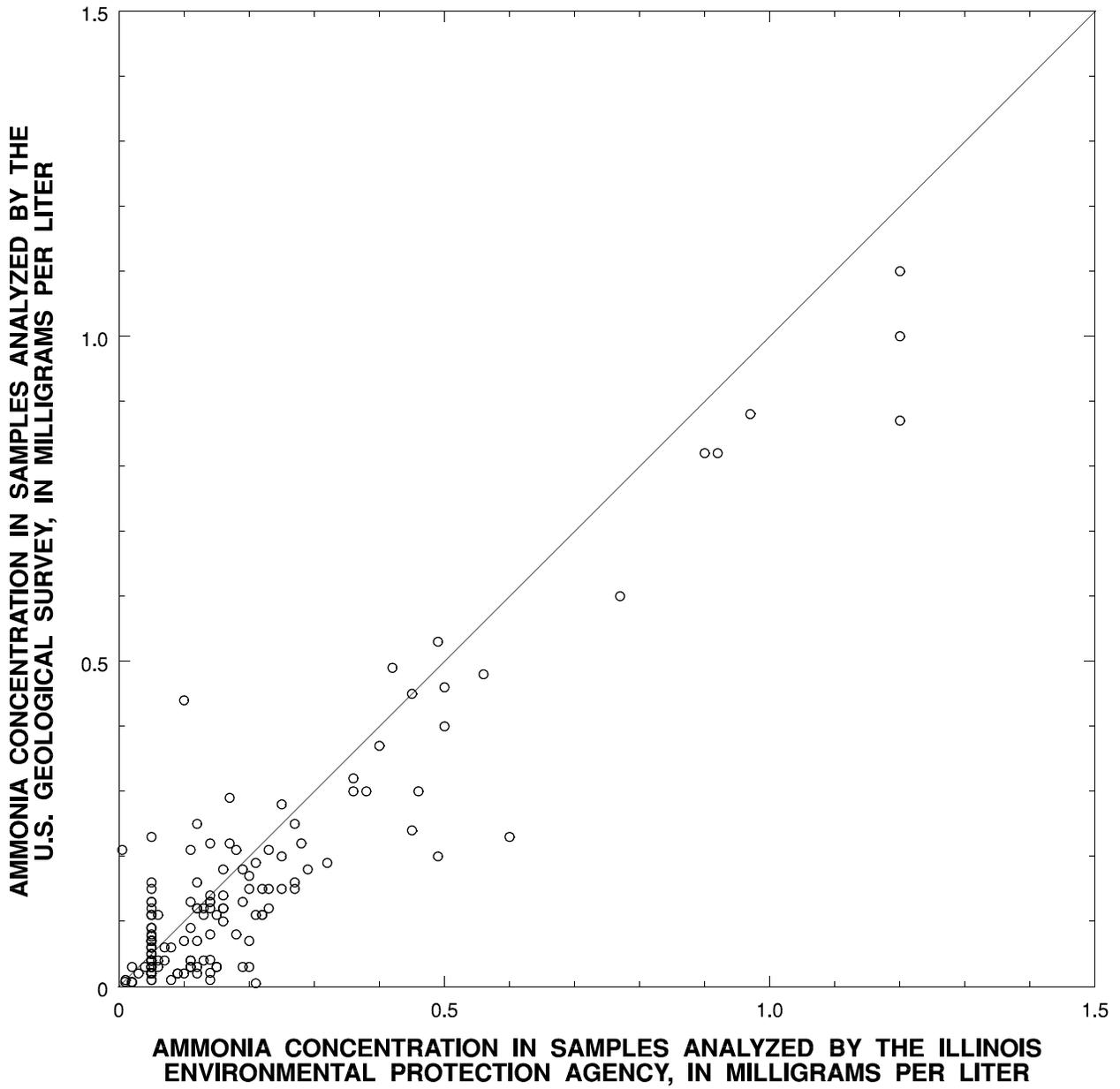


Figure 17. Ammonia concentration in paired split samples of water from Illinois streams.

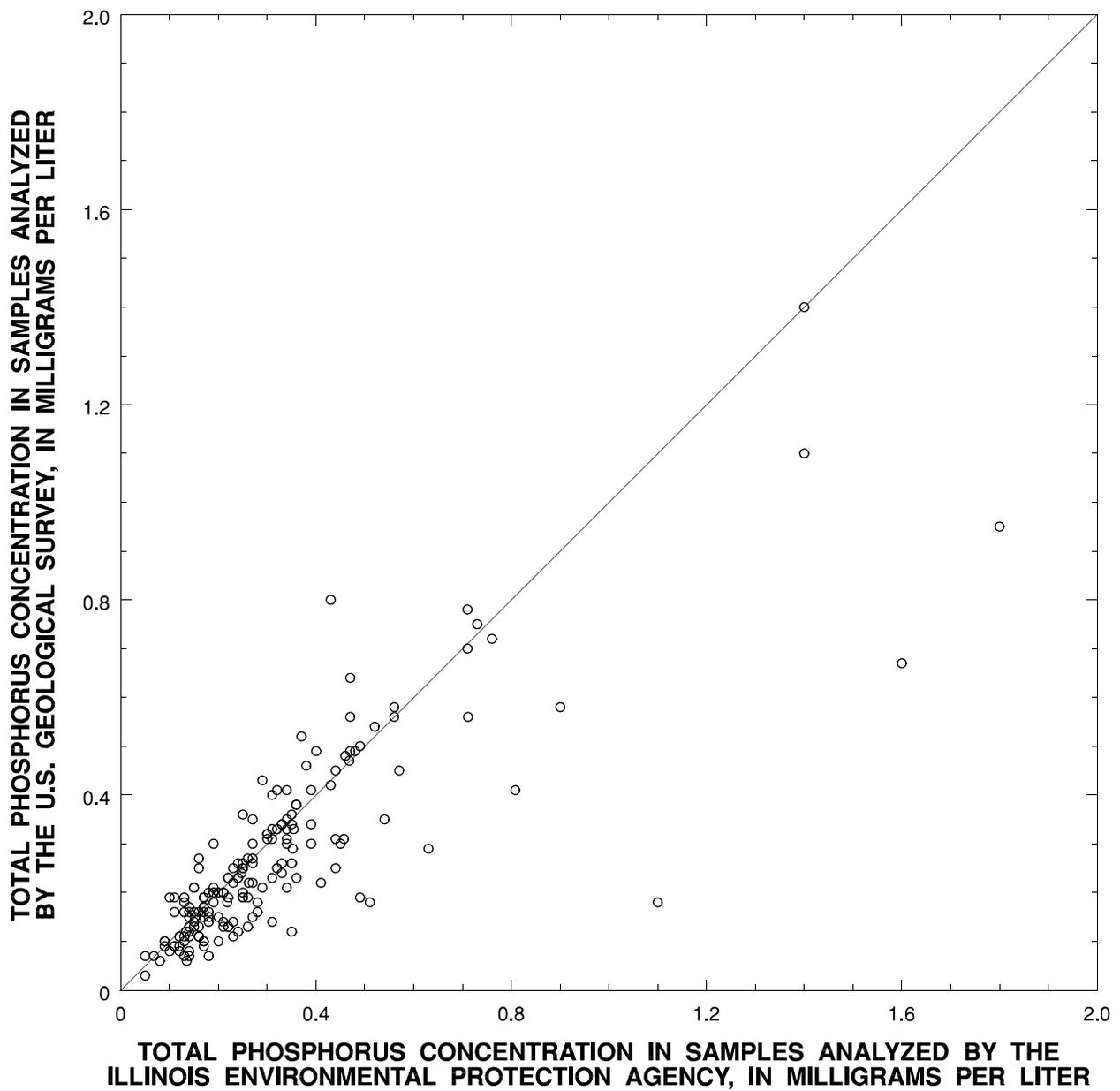


Figure 18. Total phosphorus concentration in paired split samples of water from Illinois streams.

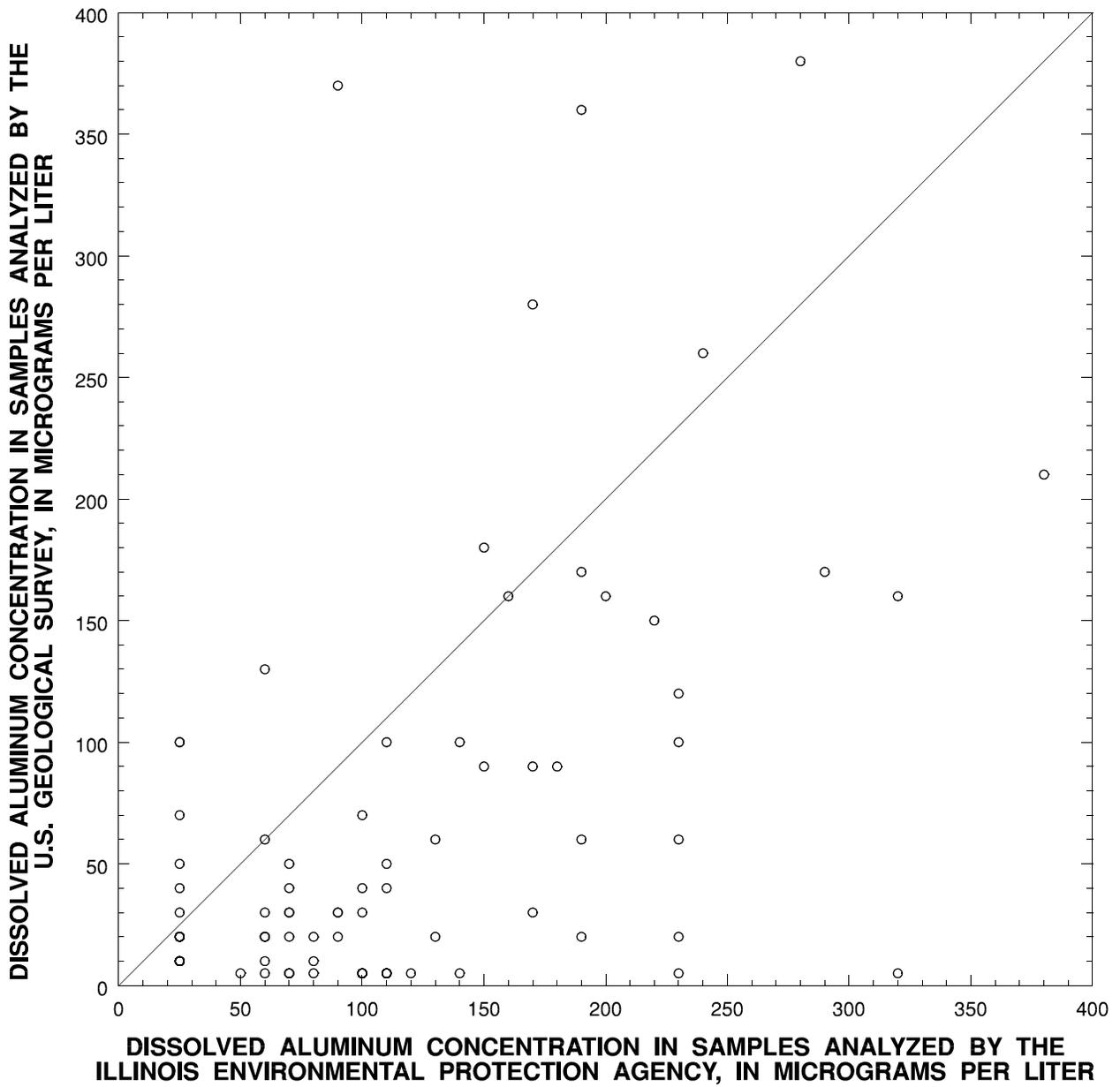


Figure 19. Dissolved aluminum concentration in paired split samples of water from Illinois streams.

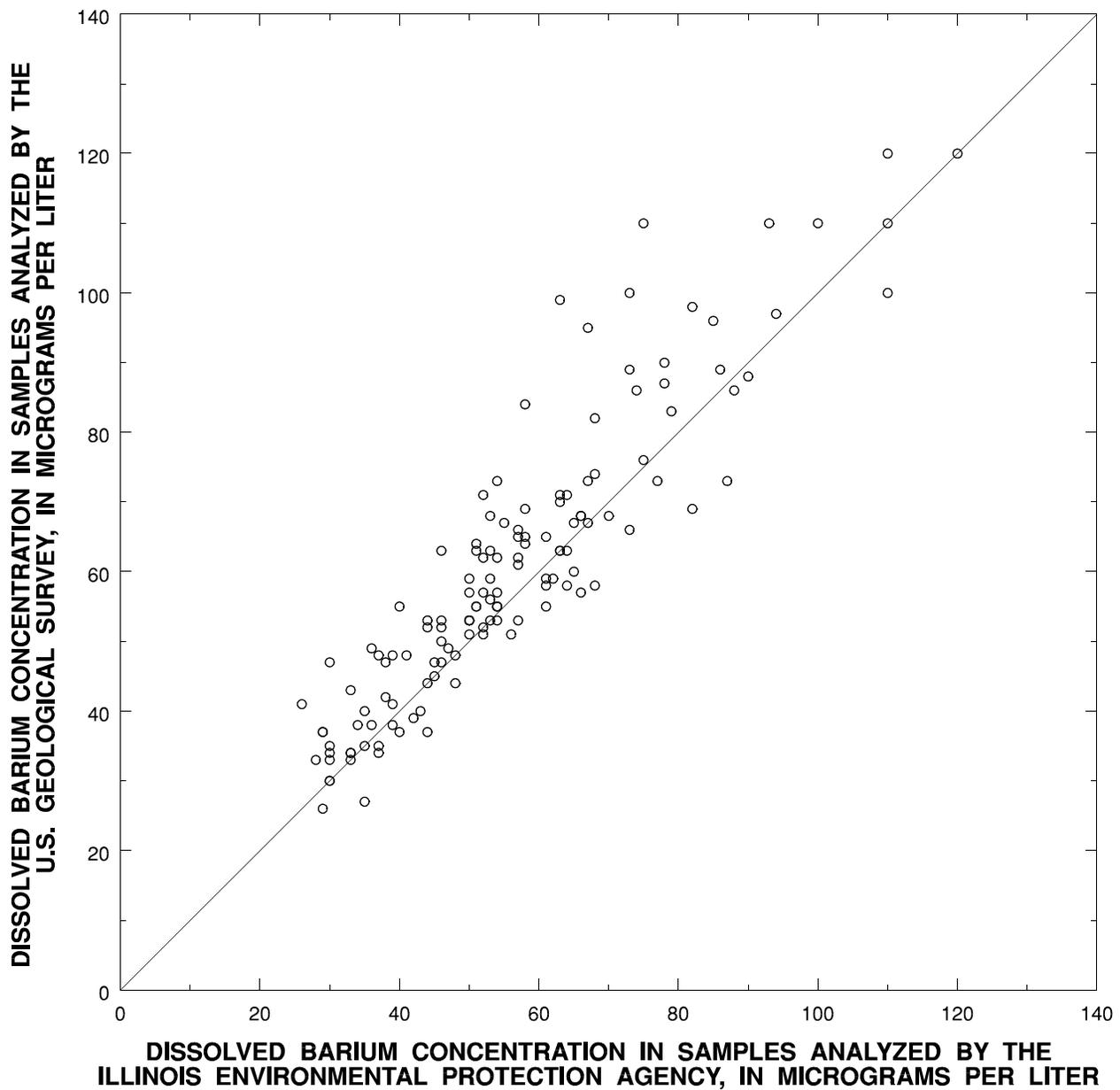


Figure 20. Dissolved barium concentration in paired split samples of water from Illinois streams.

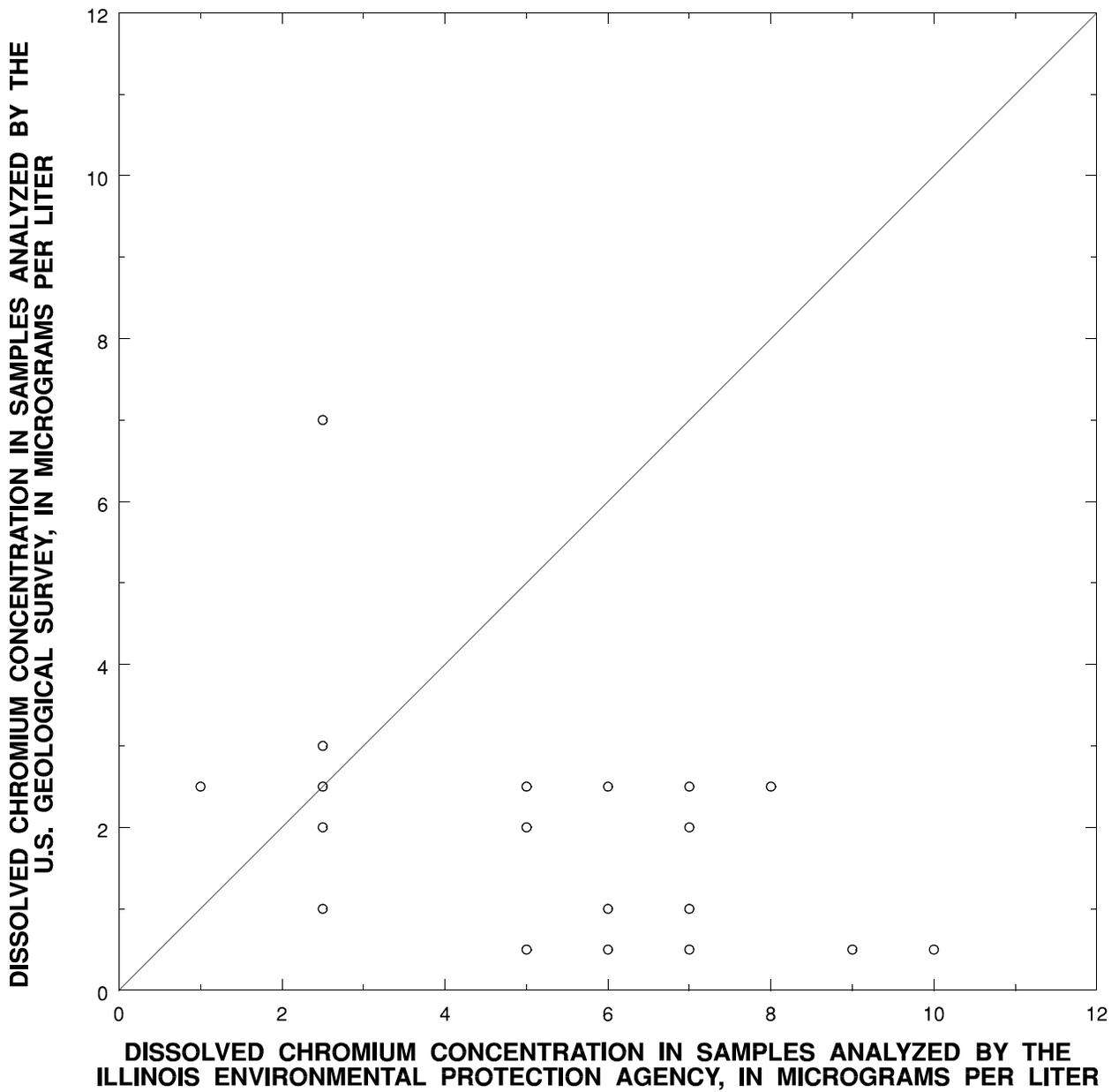


Figure 21. Dissolved chromium concentration in paired split samples of water from Illinois streams.

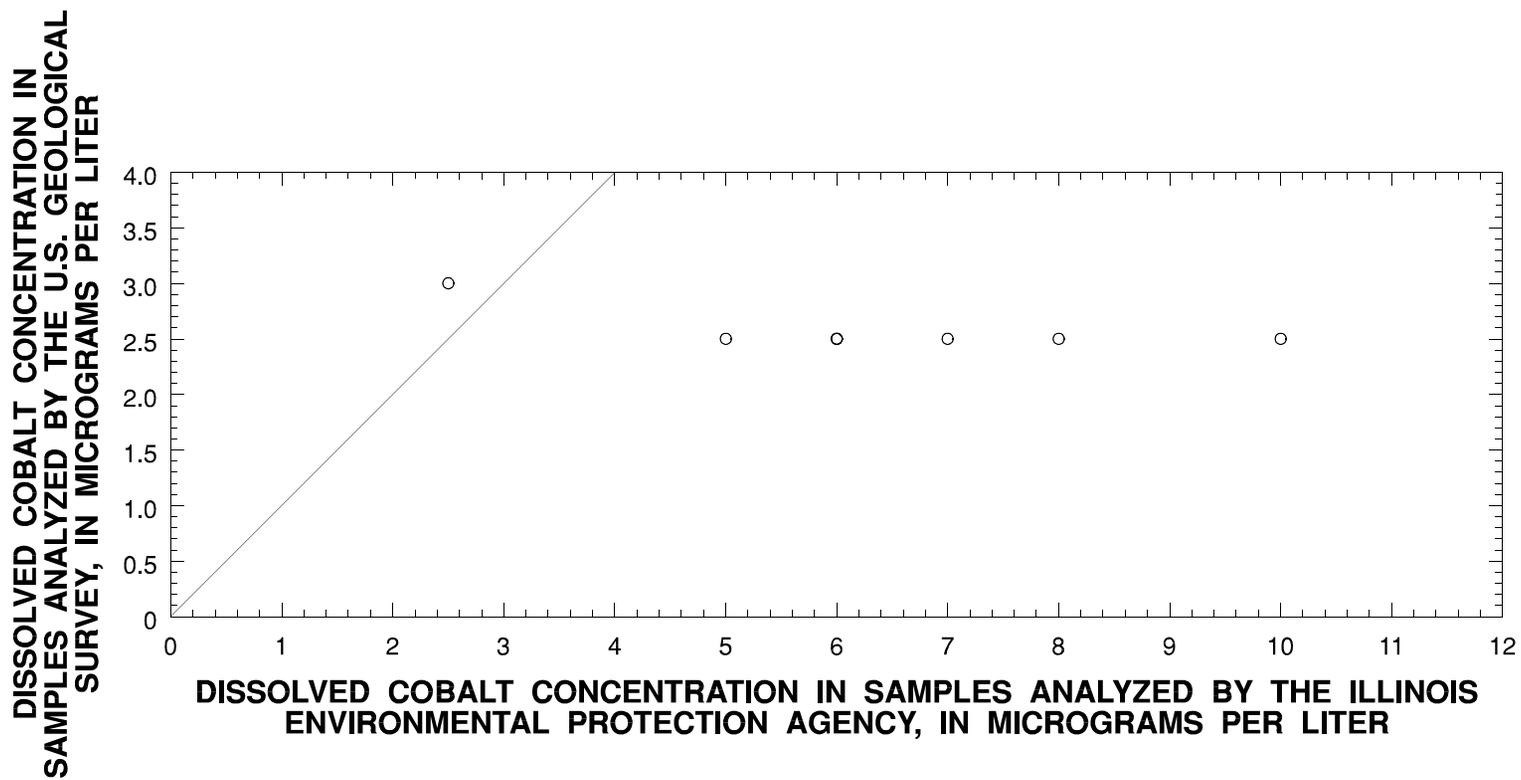


Figure 22. Dissolved cobalt concentration in paired split samples of water from Illinois streams.

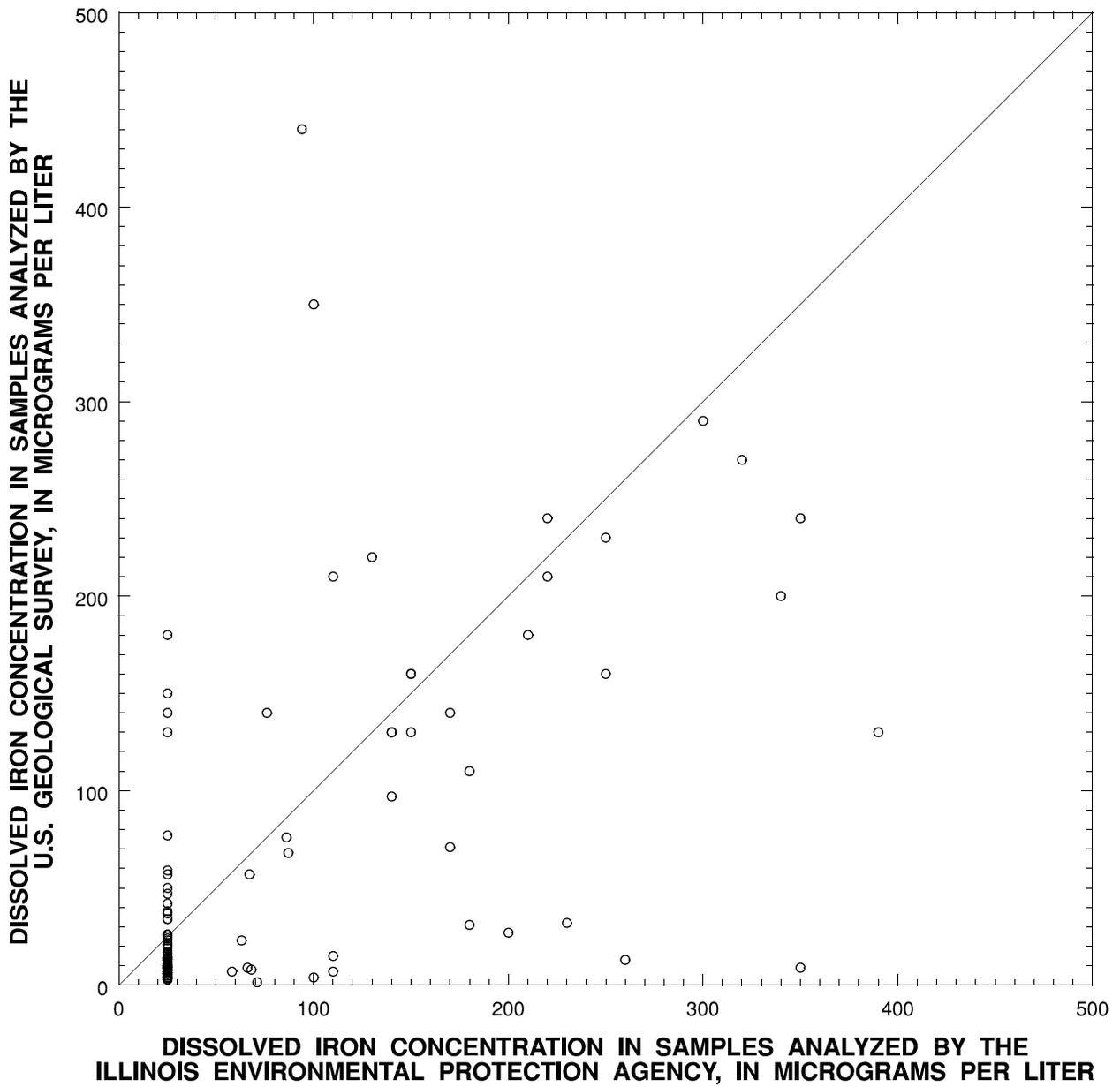


Figure 23. Dissolved iron concentration in paired split samples of water from Illinois streams.

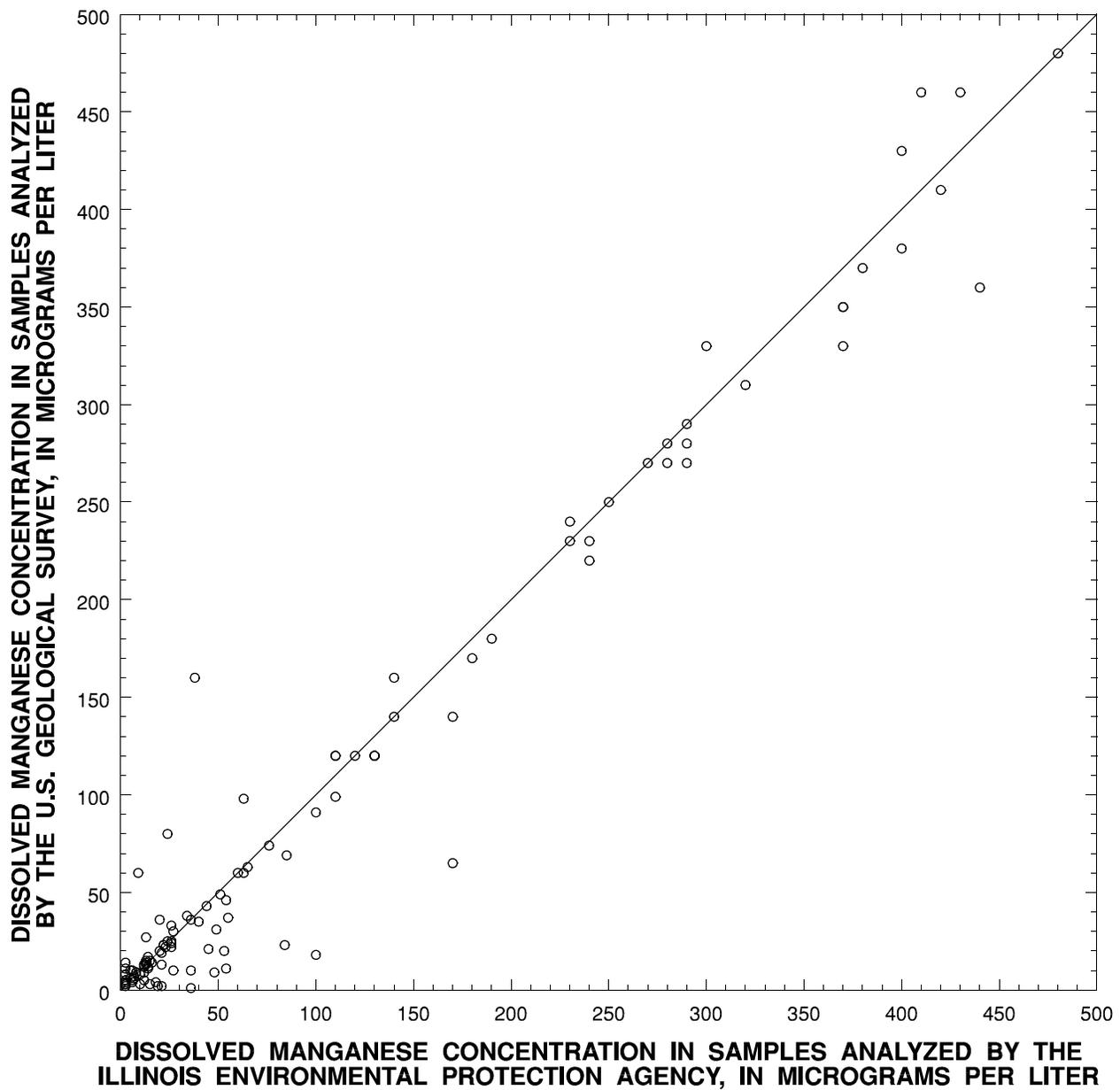


Figure 24. Dissolved manganese concentration in paired split samples of water from Illinois streams.

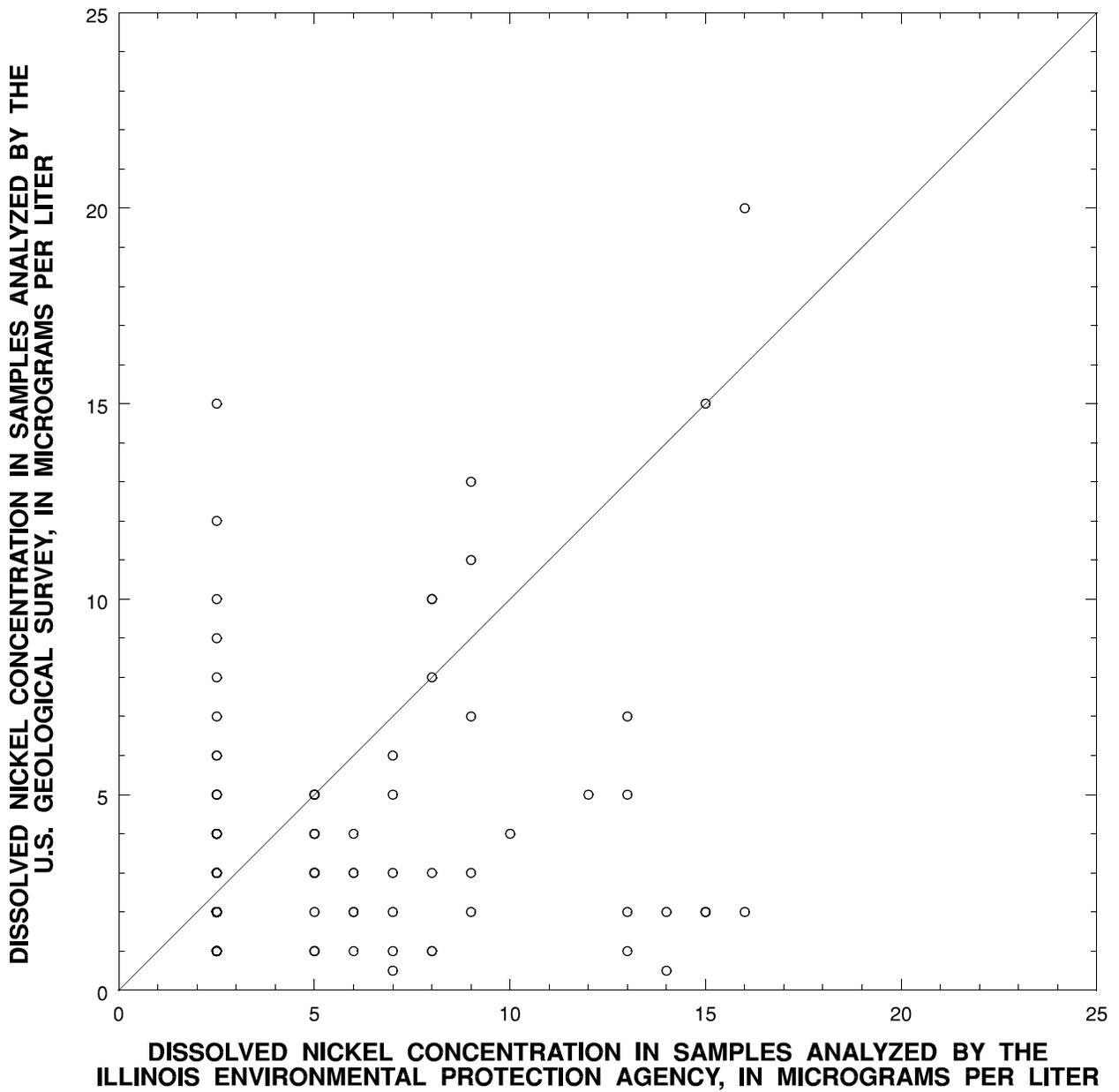


Figure 25. Dissolved nickel concentration in paired split samples of water from Illinois streams.

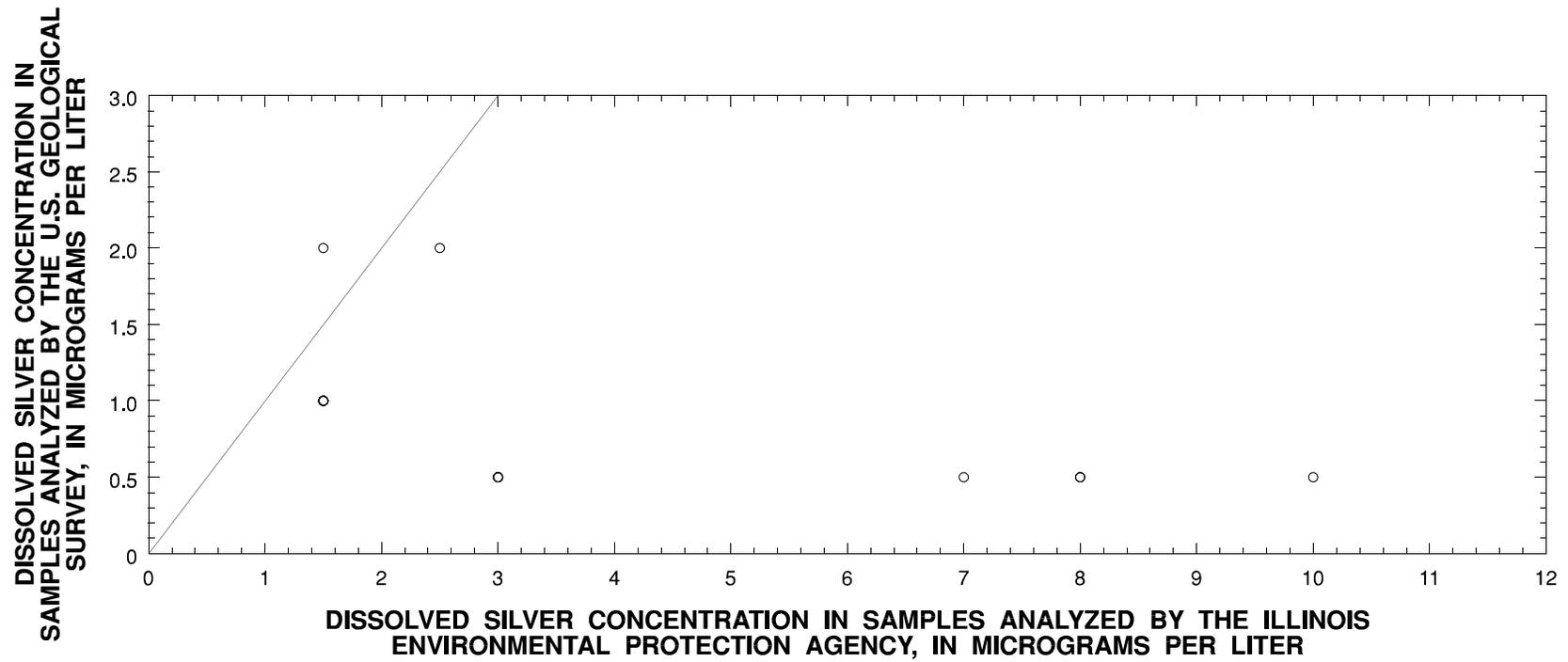


Figure 26. Dissolved silver concentration in paired split samples of water from Illinois streams.