The Interagency Pesticide Database and Pesticide Occurrence in the State's Aquifers

Abstract

The Texas Commission on Environmental Quality (TCEQ) has compiled a database, the Interagency Pesticide Database (IPD), which contains pesticide groundwater monitoring data acquired from various agencies and other entities from across the state. The development and maintenance of this database is supported by a US Environmental Protection Agency (EPA) Clean Water Act Section 106 Groundwater Grant.

The need for a statewide database that specifically addresses groundwater contamination from agricultural chemicals and agents arises from evidence nationwide that the use of these chemicals can, in some instances, lead to pollution of groundwater. The high cost of monitoring water quality statewide has necessitated that groundwater data from all available sources be gathered in one centralized location and evaluated on a statewide basis. This database contains data gathered through August 2006. The data is primarily from non-commercial sites and does not contain data from facilities subject to the Federal Resource Conservation and Recovery Act (RCRA).

Through the IPD the TCEQ has been aided in identifying areas where nonpoint-source contamination of groundwater may be occurring, information which aids in the implementation of the *Texas State Management Plan for the Prevention of Pesticide Contamination of Groundwater* (Also known as the *Pesticide Management Plan* or PMP). In support of the State PMP, the database has provided information on: 1) the occurrence of nonpoint source contamination of groundwater from the use of agricultural chemicals, 2) the occurrence of point source contamination of groundwater by agricultural practices, and 3) a computerized database that facilitates graphical, numerical, and spatial analyses of the occurrence of pesticides in groundwater.

Introduction and Background

The Interagency Pesticide Database (IPD) was initiated by the former Texas Water Commission in 1989. The need for a statewide database that specifically addresses groundwater contamination from pesticides arises from evidence nationwide that the use of these chemicals can in some instances lead to pollution of groundwater. The high cost of monitoring water quality statewide makes it prudent to first gather into one database all existing and ongoing monitoring data from all available sources. This data can then be evaluated on a statewide basis. This was first done with an unpublished report entitled *1991 Pesticides in Ground Water Database Report for Texas* (Arthur and Ambrose, 1992).

The database is the result of combining the known available data from pesticide groundwater monitoring performed by various state agencies and other entities and is primarily from monitoring activities at non-commercial sites. The IPD does not contain data from RCRA-regulated waste management facilities. The development and maintenance of this database is supported by an EPA CWA Section 106 Groundwater Grant.

The coordination for the formation and upkeep of the database is through the Agricultural Chemicals Subcommittee (ACS) of the Texas Groundwater Protection Committee (TGPC). This Subcommittee, consisting of representatives from various state agencies and other entities involved with groundwater quality and pesticides, has been valuable in providing guidance in the construction and maintenance of the database.

Purpose

The IPD aids the TCEQ and the other cooperating agencies of the ACS in identifying areas where pesticide contamination of groundwater may be occurring. This cooperative mechanism for assessing available groundwater data from all sources and thus identifying problem areas is crucial to taking steps to preventing further contamination.

Pesticide Management Plan (PMP): The goal of the PMP is to protect the existing quality of groundwater and to prevent the degradation of state groundwater resources. The PMP is a basic program consisting of a set of specific actions aimed at the prevention of groundwater pesticide contamination. It also identifies the specific roles of state and federal agencies that have various jurisdictions and responsibilities over groundwater. The Generic PMP for the state of Texas, entitled *Texas State Management Plan for Prevention of Pesticide Contamination of Groundwater*, generically outlines actions to be taken under specific conditions. The identification of areas of pesticide contamination of groundwater is an important element in the development and implementation of the PMP program.

Monitoring and Pesticide Management: Monitoring groundwater for the occurrence of pesticide contamination is a primary necessity for evaluation and then to determine what actions if any need to be taken for prevention or restoration. Analysis of the IPD will provide information as to where certain pesticides have been monitored and the results of the monitoring. Thus, it will make apparent where further monitoring may be necessary, or, if enough information is present, what types of management may be necessary in specific problem areas. The type of management necessary would be contingent on such things as the adequacy of existing monitoring data, evidence for point or nonpoint source, concentrations and toxicity of the detected pesticide or pesticides, and responsiveness of the contamination problem to any previous management efforts. The response would consist of one or more of the following: additional monitoring, implementation of a voluntary BMP program, implementation of a mandatory BMP program, or elimination of the use of the contaminating pesticide in the problem area. Assessing existing data in the IPD initiates the process of discovering any problem. It may help in making an initial evaluation of what further investigations may be necessary to determine the severity and circumstances of the contamination and establish what actions may be necessary

to manage the contamination.

Main Data Sources

The Interagency Pesticide Database (IPD) provides a mechanism for compiling and mapping pesticide groundwater monitoring data acquired from various state, federal, and other entities from across the state. State agencies, such as Texas Department of Agriculture (TDA), Texas Water Development Board (TWDB), Texas Department of State Health Services (TDSHS), and the TCEQ have conducted pesticide monitoring in the past and some continue to do so. The IPD also includes data from Federal agencies, such as from the USGS national studies on pesticides and other special studies. Local entities, such as Groundwater Conservation Districts, Public Water Supplies (PWSs), or special regional studies have also provided some data. Whenever available, groundwater pesticide data are also obtained from studies conducted by pesticide manufacturers. The seven data sources for the IPD are listed below.

The Texas Commission on Environmental Quality (TCEQ) and predecessor agencies
The United States Geological Survey (USGS)
The Texas Water Development Board (TWDB) and predecessor agencies
Pesticide Manufacturers (MANU)
The Texas Department of State Health Services (TDSHS) and predecessor agencies
The Texas Department of Agriculture (TDA)
Groundwater Conservation Districts (GWCD)

Table 1 shows, for each entity, the total number of samples (sampling events) for which data was provided. The table also shows the total number of wells sampled by each entity. Since in many cases wells were sampled on more than one occasion, the total number of wells sampled is less than the total number of sampling events.

Table 1: Data Sources

Data Source	Number of Sampling Events (Samples)	Number of Wells Sampled
TCEQ	4,047	3,131
USGS	2,393	942
TWDB	726	702
MANU	524	504
TDSHS	44	43
TDA	33	24
GWCD	23	21

Figure 1 in the Appendix shows the locations of the sampled wells, with each data contributing entity represented by a different color. Not easily ascertained from the map is the fact that a number of wells were sampled by more than one entity. Also, approximately 13.7% of the wells

with monitoring data in the IPD do not have latitude/longitude information and therefore do not appear on the map.

Structure of the Database

The IPD is in the form of a largely normalized relational database. The normalization process has necessitated that the data be divided into three separate tables: the analytical results table; the sampling event information table; and the well information table. These three tables are related through common fields. Through the normalization process, most common fields and repetitive data have been eliminated. A well in the well information table can have been sampled a number of times and thus have a number of corresponding related entries/records in the sampling event information table. Furthermore, a sample can have been analyzed for a number of analytes and thus have a number of corresponding related entries/records in the analytical results table. At the present time the database is in a state of transition by being maintained in both Paradox and Microsoft Access, but eventually it will be only updated in Microsoft Access.

Analytical Results Table: The analytical results table or analyte table contains all the chemical analysis results information. At present it contains 173,308 records. There is one entry or record for each pesticide in the suite of pesticides for which a sample was analyzed. For laboratory analyses each sample is usually analyzed for a suite of several pesticides. For immunoassay analyses, each sample was usually analyzed for two pesticides, atrazine and metolachlor. The analyte table contains fields for such information as analyte name, concentration (when there is a detection), detection limit, and quality assurance information (QA) when available. There are also two fields which relate the analyte table to the sample table and the well table, the Sample Relate field and the Well Relate field. These relational connections enable the performance of queries that require information from the other tables. The structure of the analytical results table is shown in more detail in **Figure 2**, in the Appendix.

Sampling Event Information Table: The sampling event information table, or sample table, contains all the data pertinent to each sampling event. At present it contains 8,294 records. A sampling event is defined as a visit to a well site and the taking of a sample. Information for the primary sample is entered as one record in the table. If a duplicate sample is taken it adds an additional record which is designated as being for a duplicate sample. If samples are taken for both laboratory and immunoassay analysis, each receives its own record. The sample table contains fields for such information as sample number, test method, hold time, date sampled, time sampled, sampling agency, data origin, laboratory, and program name. The Well Relate field relates the sampling table to the well table and the Sample Relate field relates it back to the analyte table. The structure of the sampling event information table is shown in more detail in **Figure 3**, in the Appendix.

Well Information Table: The well information table, or well table, contains information on each well sampled. At present it contains 5,204 records. There are fields for information such as state well number (when available), other well numbers, latitude and longitude, county, and

basin. Fields for well completion information such as aquifer, elevation, total depth, completion date, and casing diameter are also included. Additional fields for well type, well use, owner, and owner's address are also present. The Sample Relate and Well Relate fields relate the table back to the analyte and sample tables. The structure of the well information table is shown in more detail in **Figure 4**, in the Appendix. The locations of all the sampled wells for which latitude and longitude data were available are shown in **Figure 1**, in the Appendix.

Limitations on the Use of the Data in the IPD

Before proceeding with any kind of analysis of the data in the IPD it is important to recognize that the usability of the data is limited to some extent because it originates from studies or investigations designed and conducted by several different agencies and entities for various purposes and at different time periods. Ideally all monitoring activities would have been conducted under a very similar project plan, under very similar quality assurance/quality control (QA/QC), and all chemical analyses for any given analyte would have been performed using the same analytical method. The following characteristics and deficiencies of the data give an indication of some of the limitations.

- Many of the contributing agencies or entities did not include any QA/QC data with the monitoring data which they provided. In many cases this is because they did not include this information in their own database, making it very difficult to obtain at a later date. The older the data the less likely it is that QA/QC information is available. QA/QC information is important in comparing data and in drawing conclusions from the data.

- For most of the data the laboratory analysis method is not identified nor the method detection limits for the pesticide analytes. Some of the sampling data goes back to the later 1960s. There has been a steady improvement in the analytical methods since then, and the detection limits have steadily gone down. Obviously, this makes it difficult to directly compare data analyses results over the whole 1965 to 2006 time period. **Table 2** shows how groundwater pesticide monitoring activity had increased over time, and **Table 8** shows how the average detection limit has varied over time. **Figure 5** shows where monitoring occurred over time. In comparing **Figure 1** and **Figure 5** one can see that there is some correlation between data source and time period, indicating that the contributing entities would primarily be involved with a monitoring project at some particular time when there would be an interest in a particular pesticide or pesticides in some particular geographic location.

- Approximately 13.7% of the well data does not include latitude and longitude locations. This well data came with less exact indications of location and sometimes just the county was listed. Well data without latitude and longitude information is usually from older groundwater monitoring activities.

- In most cases wells have yet to be re-sampled to confirm pesticide detections. Wells with detections of pesticides at very low levels, especially at levels well below EPA's Maximum

Contaminant Level (MCL) or well below EPA's Health Advisory Level (HAL), have a very low priority for resampling. Limited financial resources allow only the highest priority well detections to be resampled for confirmation.

- A big portion of the data in the IPD is from the immunoassay analysis of groundwater samples. The TCEQ has been using immunoassay analyses as a screening method for atrazine and metolachlor. However, immunoassay analysis for atrazine detects not only atrazine but also responds in various degrees to the presence of other triazines as well as to some of the triazine metabolites when they are present. TCEQ experience has shown that, when the same water sample is analyzed by both immunoassay and laboratory Method 525, immunoassay detections of atrazine below 0.3 ppb are not detected by the laboratory analysis, even though the detection limit for atrazine, for the laboratory Method 525 is 0.10 ppb. This indicates that it may be common to have either additional triazines or degradates of triazines present when atrazine is present. This makes the immunoassay method more useful as a screening tool than a tool for the precise determination of a specific pesticide. The conclusion is that immunoassay data and laboratory data for atrazine is not directly comparable, and comparison between laboratory and immunoassay results may be questionable for metolachlor or other pesticides as well.

- Except for the immunoassay screening for atrazine and metolachlor, groundwater monitoring for pesticides in the state is still largely incomplete. From **Figure 1** we can see that a large part of the state is not covered and that the biggest coverage is from TCEQ monitoring which mostly made use of immunoassay analyses, which is considered primarily as only a screening method. So, most of the coverage is only for atrazine and metolachlor with a scarcity of data for other pesticides. Furthermore, most of the monitoring information comes from immunoassay analysis which is considered to be more useful as a screening tool than an analytical method for the precise determination of a specific pesticide.

Because of the above limitations, the data in the IPD should be used with caution. Inferences should be made only after careful consideration of all the limiting factors. A certain expertise will be necessary to make a proper use of data of such varying quality and obtained under such varying circumstances. A casual user could quickly run into difficulties in using such an assortment of data that may be unsuitable for many types of analyses. Any conclusions drawn from the data should be qualified by carefully citing all the limiting factors that may be pertinent.

Analysis of IPD Data

One of the advantages of having data in a database is that it can be queried in an almost unlimited number of ways to extract useful information. With GIS capabilities the extracted data can be displayed in a graphical format, further enhancing the analyses that can be performed and thus what can be learned from the database. A discussion of the various analyses that were performed on the data follows.

Table 2: Monitoring Activity Over Time

Time Period	Number of Sampled Wells	Number of Samples
≥ 1960, < 1970	27	31
≥ 1970, < 1980	171	222
≥ 1980, < 1990	769	1,180
≥ 1990, < 2000	1,288	1,991
≥ 2000	3,325	4,364

Detected Pesticides: This category includes records of both confirmed and unconfirmed detections for all pesticides. Duplicate samples taken for QA purposes are excluded. **Table 3** shows a listing of the pesticides in the IPD for which there were detections, in order of most often detected to least detected. The most often detected pesticide was atrazine with 279 detections. Atrazine is one of the pesticides of concern for possible groundwater contamination, listed by EPA in their *Pesticides and Ground Water State Management Plan Regulation; Proposed Rule*[7]. The other three pesticides on the list include metolachlor, alachlor, and simazine. Simazine appears in **Table 3** in forth place with 82 detections and metolachlor seventh with 35 detections. Triazine metabolites appear n second place, being detected in 157 different wells and springs.

Figure 6 shows the geographic distribution of detections for each pesticide. The map shows two areas that have an obvious pattern of pesticide occurrence. The Edwards aquifer area shows a definite pattern of incidents of detection of a number of pesticides. The probable main reason for the occurrence of pesticides here is because the Edwards is a karst aquifer. A karst aquifer is one made up of fractured limestone with the presence of underground voids and cavities. The fractures provide an easy path for the transport of pollutants such as pesticides to the aquifer. Another corresponding reason for the large number of detections here is that, since the vulnerability of the aquifer is well established, it has become a target of a number of monitoring efforts. Thus a relatively large number of wells have been sampled for pesticides in the area as compared to most other areas of the state. Also, some of the monitoring was done by the USGS whose analyses generally have very low detection limits. Low detection limits tend to increase the number of detections. The most common detections were for atrazine, triazine metabolites, prometon, simazine, and diazinon.

There is also a rather large area in the Panhandle that has a pattern of pesticide occurrence. The predominant pesticide detected here, as in the Edwards Aquifer, was atrazine. Another triazine, propazine, was also detected on a number of occasions. This area has undergone considerable monitoring over the last few years after atrazine was first detected in some of the public water supply systems. During much of this time, the TCEQ has made at least one monitoring trip per year to this area of the Panhandle, sampling a number of wells which consistently analyze positive for atrazine. More recently TCEQ has decreased the frequency of its pesticide monitoring visits to the Panhandle.

Table 3: Pesticide Detections in the IPD

Pesticide Analyte	Number of Wells and Springs
Atrazine	279
Triazine Metabolites	157
Prometon	92
Simazine	82
Diazinon	47
Propazine	35
Metolachlor	35
2,4-D	29
Bromacil	23
p,p'-DDE	22
Dichloropropane	18
Carbaryl	11
Tebuthiuron	11
Diuron	9
Alachlor	7
Heptachlor epoxide	7
Hexazinone	7
Terbacil	7
Dieldrin	6
p,p'-DDT	6
Other	150

Included under Other, an additional 66 other pesticides were detected, ranging from five detections each down to one. The total number of detections was 1,038.

Confirmed Detections of Pesticides: This analysis includes only cases of the presence of pesticide in groundwater confirmed by chemical analysis. A confirmation, for the purposes of this analysis, was defined as one or more subsequent detections of a pesticide in a well or spring, by either a laboratory or immunoassay method chemical analysis, after an initial detection of the same pesticide, by either laboratory or immunoassay method. **Table 4** shows a listing of pesticides that were confirmed to be present and the number of wells and springs for which they were confirmed.

This analysis is more significant than the one for total number of detections, because very often a detection is proven to be fleeting. The presence of the pesticide could have been due to a localized contamination that has since dispersed or degraded, or the original pesticide analysis could have rendered a false positive. Atrazine, which was confirmed to be present in 89 wells, is again shown to be the pesticide most present in groundwater in the state. **Figure 7** shows the geographic distribution of the confirmed detections. The confirmed detection map shows the same two areas with patterns of atrazine contaminated groundwater as was shown by the map depicting all pesticide detections, namely the Edwards Aquifer area and the Ogallala Aquifer area in the Panhandle.

Table 4: Confirmed Detections in the IPD

Pesticide Analyte	Number of Wells and Springs
Atrazine	89
Triazine Metabolites	34
Simazine	21
Prometon	18
Propazine	12
Metolachlor	6
2,4-D	5
Diazinon	5
Carbaryl	4
Fipronil	4
Metribuzin	3
Terbacil	3
1,2-Dichloropropane	2
Imidacloprid	2
Other	10

Combined under Other are Bromacil, Clorpyrifos, 1,3-Dichloropropene, Endrin, Heptachlor epoxide, Hexazinone, Imazaquin, Naphthalene, Tebuthiuron, and p,p'-DDE, which had one confirmed detection each. The total number of confirmed detections was 218.

Concentration Ranges of the Three Most Detected Pesticides: Atrazine, triazine metabolite, simazine, prometon, propazine and metolachlor were the six most detected pesticides with confirmed detections. **Table 5** shows the concentration ranges for these pesticides. Atrazine has four detections above the MCL of 3.0 µg/L. Triazine metabolites, which are a group of compounds, do not have an MCL or HAL, but all detections for them were at a very low level, below 0.1 µg/L. Simazine has an MCL of 4.0 µg/L. All the detections of it were well below that concentration. Both prometon and propazine have HALs of 100 µg/L. Detections for both of them were well below this HAL. Metolachlor has an HAL of 700 µg/L. None of the metolachlor detections come even close to its HAL.

Sources of Confirmed Detections Data: Table 6 shows the total number of confirmed detections per data source. There were five entities that provided pesticide groundwater monitoring data which included confirmed detections. These were the TCEQ, TWDB, USGS, TDA, and one GWCD. The USGS provided the most with 139 confirmed pesticide detections, and TCEQ was second with 72 confirmed pesticide detections. TDA had five confirmed pesticide detections. The TWDB and the GWCD each had only one confirmed detection. Atrazine or metabolites of a triazine were the most detected analytes.

Figure 8 shows the geographic breakdown of where the detections were located for each of the entities that provided data for confirmed detections. **Figure 8** when used in conjunction with **Figure 7** will also indicate which pesticides were detected by each entity. The TCEQ was the most responsible for providing monitoring data of confirmed detections in the Panhandle area.

Many of these samples were provided by the TWDB and then analyzed by TCEQ using immunoassay. (See the discussion on Cooperative Monitoring below.) The TWDB and the USGS were most involved with groundwater pesticide monitoring that confimred detections of pesticide in the Edwards Aquifer.

Table 5: Range of Confirmed Atrazine Detections

Concentration Range, ppb	Number of Detections
Atrazine (MCL = 3.0 µg/L)	
≥ 0.0, < 0.1	32
≥ 0.1, < 0.5	25
≥ 0.5, < 1	18
≥ 1, < 2	7
≥ 2, < 3	3
≥ 3, < 4	1
≥ 4, < 5	1
≥ 5	2
Triazine Metabolites (No MCL or HAL)	
≥ 0.0, < 0.05	31
≥ 0.05, < 0.1	3
≥ 0.1	0
Simazine (MCL = 4.0 µg/L)	
≥ 0.0, < 0.05	21
≥ 0.05	0
Prometon (HAL = 100.0 µg/L)	
≥ 0.0, < 0.05	14
≥ 0.05, < 1	1
≥ 1, < 2	1
≥ 2, < 10	1
≥ 10, < 100	1
≥ 100	0
Propazine (HAL = 100.0 µg/L)	
≥ 0.05, < 0.1	4
≥ 0.1, < 0.5	3
≥ 0.5, < 1	3
≥ 1, < 100	2
≥ 100	0
Metolachlor (HAL = 700.0 µg/L)	
≥ 0.0, < 0.1	1
≥ 0.1, < 0.5	4
≥ 0.5, < 2	1
≥ 2	0

Table 6: Confirmed Detections per Data Source

Pesticide Analyte	Number of Detections
USGS	
Triazine Metabolite	34
Atrazine	33
Simazine	21
Prometon	15
Diazinon	5
2,4-D	4
Carbaryl	4
Fipronil	4
Metribuzin	3
Terbacil	3
1,2-Dichloropropane	2
Imidacloprid	2
1,3-Dichloropropene	1
Bromacil	1
Chlorpyrifos, (Dursban)	1
Hexazinone	1
Imazaquin	1
Metolachlor	1
Naphthalene	1
Tebuthiuron	1
p,p'-DDE	1
Total:	**139**
TCEQ	
Atrazine	54
Propazine	12
Metolachlor	5
Heptachlor epoxide	1
Total:	**72**
TDA	
Prometon	3
Atrazine	2
Total:	**5**
GWCD	
2,4-D	1
Total:	**1**
TWDB	
Endrin	1
Total	**1**
Grand Total:	**218**

Concentration Trends: The IPD has enough data on a number of wells and a few springs which have been sampled enough over a period of time that trend analyses could be performed. For the trend analyses four springs were chosen and twelve wells. Information on these wells and springs is shown in **Table 7**.

Table 7: Well and Spring Information for Concentration Trends

State Well Number	Spring Number	Description	Latitude	Longitude	Sampling Entity
	08155395	Upper Barton Springs at Austin, TX	N/A	N/A	USGS
	08155500	Barton Springs at Austin, TX	N/A	N/A	USGS
	08155501	Eliza Spring at Austin, TX	N/A	N/A	USGS
	08155503	Old Mill Spring at Austin, TX	N/A	N/A	USGS
1013537		City of Hereford, (Well #19)	34.8016660	-102.4191660	TCEQ
1013612		City of Hereford, (Well #11)	34.8111110	-102.3930550	TCEQ
1013613		City of Hereford, (Well #12)	34.8169430	-102.3772210	TCEQ
1019711		City of Friona, (Well #9)	34.6341660	-102.7211100	TCEQ
1019712		City of Friona, (Well #10)	34.6302778	-102.7269444	TCEQ
1030511		City of Dimmitt, (Well #I9)	34.5422222	-102.3111111	TCEQ
1038503		City of Dimmitt, (Well #KS2)	34.4494444	-102.3005556	TCEQ
1038504		City of Dimmitt, (Well #LS3)	34.4483333	-102.2952778	TCEQ
1038604		City of Dimmitt, (Southfield Well #4)	34.4491667	-102.2919444	TCEQ
1126920		City of Tulia, (Well #9)	34.5183333	-101.7619444	TCEQ
1126921		City of Tulia, (Well #10)	34.5177778	-101.7658333	TCEQ
1151416		City of Plainview, (Well #16)	34.1755556	-101.7105556	TCEQ

Four springs were sampled repeatedly by the USGS over a period of time, mostly between 2000 and 2007. The USGS over this time period analyzed for atrazine and triazine metabolites. The triazine metabolite concentration trends are plotted in **Figure 10** and the atrazine concentration trends in **Figure 11**. The plots show no discernable long term concentration trends for any of the four springs. Springs 08155500 and 18155395 show much more volatility than 08155501 and 08155503. This could be because 08155500 and 18155395 have easier channels of communication between their source water and the contributing areas of atrazine application. It is also possible that there is a more intense usage of atrazine in the contributing areas for these two springs.

In performing PMP monitoring in the Panhandle of Texas the TCEQ has sampled several wells that have tested positive for atrazine. Twelve of these wells have been sampled enough over a period of time to provide sufficient data for trend analyses. Some of these wells were sampled as early as 1997 and some as late as 2006. The atrazine analyses for these twelve valves is plotted out in **Figure 12**. For this analysis data from immunoassay analyses and laboratory analyses have been plotted together. Even though **Figure 12** shows a lot of variation between years and seasons for any particular well, with the variation being more extreme for some of the wells, one can still distinguish a definite trend toward lower concentrations of atrazine.

Detection Limits Verses Number of Detections: It would be reasonable to assume that the lower the detection limit for an analytical method the more likely it would be able to pick up any presence of an analyte. Furthermore, one would expect that on average analytical methods have improved over the years such that detection limits would have decreased over time. This is proven out specifically by the USGS's National Water-Quality Assessment (NAWQA) Program, implemented in 1991, in which most of the analyses are done using methods that have detection limits in the parts per trillion range. This reduction in detection limits would then be an additional reason, in addition to the increase in monitoring activity, for the increase in pesticide detections in recent years. To test the hypothesis an analysis was done on the database to determine if indeed there was a reduction in average detection limits over time. So as to be able to make meaningful comparisons, the averages were done on the same time periods as used in other analyses such as in **Table 2** above. In the analysis only data that had entries for detection limits were used. Much of the earlier data has no detection limit information which means that the averages for the earlier time periods are based on a much smaller sample base. **Table 8** shows the results of the analysis. The expected reduction in detection limits is seen for the last three time periods, but the first two time periods don't follow the expected pattern. The suspected reason for this is that the early detection limit data is too sparse to provide meaningful averages.

Number of Confirmed Detections Over Time: Table 9 below shows an increase in confirmed detections over time. When one looks at **Table 2** or **Figure 5** one can see that there was a tremendous increase in monitoring activity over time. This would be the primary explanation for the increase in confirmed detections. An additional reason would be that detection limits have gone down in recent years as analytical methods have improved. **Figure 9** shows the increase in the detections over time as well but gives a geographic perspective. One can see that most of the more recent detections have been in the Panhandle. When compared with **Figure 8**, which shows the data sources, one can see that most of the recent detections were from monitoring data obtained from the TCEQ.

Types of Pesticides Detected Over Time: There has also been some change in the types of pesticides that have been detected over time. Atrazine, even though it was widely used even before 1970 was not confirmed to be present in a well until in the 1980s. There is no data in the IPD for any atrazine analysis until 1966, and there are only records for 14 analyses for atrazine before 1990. **Table 10** shows the breakdown by decade for the pesticides with confirmed detections.

Table 8: Detection Limits Over Time

Contributing Agency	Number of Detection Limits in Average	Average Detection Limit (ppb)
< 1970		
TWDB	42	
USGS	24	
Total:	**66**	**1.33**
>= 1970, < 1980		
TWDB	182	
TDH	6	
Total:	**188**	**2.02**
>= 1980, < 1990		
USGS	12,907	
TWDB	910	
TCEQ	416	
TDH	56	
GWCD	22	
Total:	**14,311**	**2.21**
>= 1990, < 2000		
USGS	52,550	
TWDB	19,171	
TCEQ	2,111	
Manufacturers	84	
GWCD	7	
TDH	6	
Total:	**73,929**	**1.63**
>= 2000		
USGS	63,826	
TCEQ	10,640	
TWDB	12	
Total:	**74,478**	**0.13**

Table 9: Confirmed Detections Over Time

Time Period	Number of Confirmed Detections
< 1970	0
≥ 1970, < 1980	2
≥ 1980, < 1990	13
≥ 1990, < 2000	60
≥ 2000	143

Table 10: Confirmed Detections by Pesticide Over Time

Pesticide Analyte	Number of Confirmed Detections	Pesticide Analyte	Number of Confirmed Detections
≥ 1980, < 1990			
2,4-D	3	Atrazine	1
1,2-Dichloropropane	1	Prometon	1
1,3-Dichloropropene	1		
			Subtotal: 7
≥ 1990, < 2000			
Atrazine	8	Bromacil	1
Prometon	4	Chlorpyrifos, (Dursban)	1
Metribuzin	3	Endrin	1
2,4-D	2	Heptachlor epoxide	1
Carbaryl	2	Metolachlor	1
1,2-Dichloropropane	1	Naphthalene	1
			Subtotal: 26
≥ 2000			
Atrazine	80	Terbacil	3
Triazine Metabolite	34	Carbaryl	2
Simazine	21	Imidacloprid	2
Prometon	13	Hexazinone	1
Propazine	12	Imazaquin	1
Diazinon	5	Tebuthiuron	1
Metolachlor	5	p,p'-DDE	1
Fipronil	4		
			Subtotal: 185
			Total Number of Wells with Confirmed Detections: 218

Point Source Verses Nonpoint Predictions: A question that would be useful to answer from the IPD is whether or not a particular contamination is from a point or nonpoint source. Nonpoint-source contamination is typically widespread and cannot be traced back to a single origin or source. It includes pollution from such things as storm water runoff, water runoff from urban areas, and failed septic systems. It also includes contamination from agricultural activities such as the application of pesticides to cropland. Applied pesticides can, under some circumstances, infiltrate through the root zone and down into the underlying aquifer. Since this happens over a wide area, and because the contamination most often results from incremental infiltrations into the aquifer as a consequence of repeated applications of the pesticide, it is considered to be nonpoint source contamination. The Clean Water Act (CWA) defines point source as a contamination that originates from "any discernable, confined and discrete *conveyance*, including but not limited to any pipe ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other *floating craft from which pollutants are or may be discharged*." A point source pesticide groundwater contamination would usually be the result of a pesticide application, spill, or backflow that would cause pesticide to flow either down the well bore or down the outside of the well casing, usually of a poorly constructed, deteriorated, or abandoned well.

A point source contamination would be suspected if the contamination was found in one well but in no other wells in the vicinity. Or a point source would be suspected if a small number of wells are contaminated if the wells are situated such that they may be engulfed by a plume of pesticide contamination resulting from a suspected point source.

A nonpoint source would be suspected if a large number of wells would be contaminated over a fairly large area. It would be counter indicative if there is a significant number of non contaminated wells, completed in the same formation, between the contaminated wells. In such a situation the interspersed uncontaminated wells would indicate that the contaminated wells may have been affected each by a point source contamination. This would indicate that the general quality of well construction in the area is poor, thus allowing for easy point source contamination.

The strongest evidence for nonpoint source contamination is in the Panhandle, where there have been a large number of confirmed detections of atrazine. However, the evidence is not conclusive since not enough wells can be found close enough together to prove a continuum of contamination as would be present with nonpoint contamination. And when a number of wells close together are found to be contaminated, the circumstances do not exclude the possibility of a plume that could have resulted from a point source.

Major Sampling Programs

The pesticide groundwater monitoring performed by the various entities that have contributed data to the IPD has largely taken place in the context of some program undertaken to achieve some predetermined purpose. These programs are generally consistent with the normal work and

purpose of the agency that is carrying them out. Discussed briefly here will be only the major programs of some of the contributing entities.

USGS: The USGS, in carrying out its goals as a federal agency, has carried out pesticide groundwater monitoring over a long period of time. It's most recent program, under which considerable groundwater monitoring has taken place in Texas, is the National Water-Quality Assessment (NAWQA) Program. The USGS implemented the NAWQA Program in 1991 to develop long-term consistent and comparable information on streams, rivers, groundwater, and aquatic systems in support of national, regional, State, and local information needs and in support of decisions related to water-quality management and policy. Groundwater monitoring, a large part of this program, has included monitoring for pesticides. USGS data is procured periodically for the IPD as it becomes available.

TWDB: The TWDB is very involved with groundwater monitoring. They employ a number of personnel whose main job is to travel the state sampling wells. They monitor a different area of the state each year such that every five years they cover the whole state. Because of limited financial resources they seldom monitor for pesticides but concentrate on the standard water quality constituents. However, there have been some periods in the past where they have monitored for pesticides, and this data has been incorporated into the IPD.

TCEQ: The TCEQ monitors or, more often, requires the monitoring of groundwater whenever contamination has been discovered or there is a potential of contamination. Sometimes pesticides are involved. More recently, motivated by EPA's *Pesticides and Ground Water Strategy* published in 1991, the TCEQ embarked upon the implementation of a Pesticide Management Plan. This plan is described under the **Purpose** section above. This program required as one of its components the monitoring of groundwater for pesticides. Through the support of an EPA Grant, the TCEQ has undertaken a pesticide groundwater monitoring program.

Under this program TCEQ personnel have monitored several areas of the state based on groundwater susceptibility to pesticide contamination and on the discovery of the presence of pesticides, primarily atrazine, in public water supplies (PWSs). Pesticides were discovered in PWSs through the normal monitoring required by the Water Supply Division of the TCEQ. The pesticide detections were at very low concentrations, usually well below the MCL. What made some of the detections possible was the decrease in detection limits that have came with improved analytical methods in recent years. These detections of pesticides were followed up by confirmation monitoring carried out by TCEQ under their Pesticide Management Plan Activities. If the presence of pesticide is confirmed, an investigative monitoring program is implemented. If the investigative monitoring reveals a definite pesticide contamination, monitoring of the groundwater in the area is carried out once or twice a year, and this follow-up monitoring is continued until the contamination is resolved.

Chemical analyses for the Pesticide Management Plan monitoring described above is performed in one of two ways. Most of the samples undergo analysis for atrazine and metolachlor using an immunoassay technique. The immunoassay analyses provide a low cost method of screening for

these two pesticides. Results of the immunoassay analyses determine what subgroup of samples is then sent for laboratory analysis.

Immunoassay analysis has proven especially useful in a Cooperative Program entered into with the TWDB. Since TWDB personnel in their ongoing routine monitoring activity are visiting a large number of wells (See the **TWDB** section above.), they can, in addition to their standard sample set, easily capture an additional small sample for immunoassay analysis. These extra samples are transferred to the TCEQ for the immunoassay analysis for atrazine and metolachlor. This cooperative program has proven to be very beneficial in screening the state for these two pesticides. The Cooperative Monitoring Program has provided a large amount of data for the IPD.

TDA: The TDA is rarely involved with any kind of monitoring of groundwater. However, being the lead agency for pesticide regulation in Texas, they did implement a special program between 1987 and 1990, where they monitored certain counties for the presence of pesticides, nitrates, and arsenic in groundwater. The program was designed to study the potential effects of agricultural chemicals on groundwater quality. This monitoring program has provided some data for the IPD including some confirmed detections as shown in **Table 6**.

Summary and Conclusions

The IPD has made it possible to draw together groundwater pesticide monitoring data from a wide variety of sources. Since groundwater monitoring and pesticide analysis are both expensive undertakings, this combined database has served as a means of pooling resources and achieving a monitoring coverage that would be difficult to accomplish by any one agency or entity. However, even with some level of accomplishment in this area, the IPD still has some shortcomings, primarily the lack of coverage for most pesticides and the lack of consistent data quality.

The IPD is especially suitable for aiding in a program such as the PMP. The PMP requires knowledge of the state of pesticide contamination of groundwater and calls for the development and implementation of monitoring programs to increase the available data on pesticides in groundwater. In implementing the PMP, the IPD enables the initial evaluation of where problem pesticides may be getting into the groundwater, and when further monitoring is implemented under the PMP, it acts as a repository for the data.

Several temporal and spatial analyses were performed on the data. One observation is the tremendous increase in pesticide monitoring over the years. Correspondingly, one can see that there has been an increase in pesticide detections, especially atrazine. Since atrazine has been in heavy use throughout the time period spanned by the data in the IPD, the increase is probably mostly due to intensified monitoring specifically for the compound, the greater interest in monitoring being due to an increased awareness of its proclivity to leach through the root zone. However, another important factor in its greater detection is the improvement in analytical methods especially in the lowering of the detection limit.

For maximum usefulness it is important that data coverage be dense enough to help distinguish between point and nonpoint source contamination. As discussed above in the subsection, **Point Source Verses Nonpoint Predictions**, monitored wells need to be close enough together to either define a plume from a point source or to determine if there is a continuum of contamination over a wide area which would indicate a nonpoint source.

The IPD does not contain enough data on most pesticides and it is especially inadequate on areal coverage. Through the PMP program the whole state has been screened for the presence of atrazine and metolachlor in groundwater, under a cooperative monitoring program using immunoassay analysis. However, as discussed in the **Limitations of Data in the IPD** section, the immunoassay method has certain limitations in specificity. Ideally, if resources would be available, a group of pesticides of concern would be selected and the whole state systematically monitored.

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3. Cherepon, A., Musick, S., Peters, J., Groundwater Monitoring for Atrazine in the Texas Panhandle, TNRCC Environmental Trade Fair & Conference, Austin, Texas, May 2001, Proceedings Vol. 2, Pp. 409 - 419.

4. EPA, 1991(July), Protecting the Nation's Ground Water: EPA's Strategy for the 1990's, The Final Report of the EPA Ground-Water Task Force, EPA 21Z-1020. 85 Pages.

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6. EPA, 1993(December), Guidance for Pesticides and Ground Water State Management Plans, EPA 735-B-93-005a. 43 Pages.

7. EPA, 1996(June 26), Pesticides and Ground Water State Management Plan Regulation; Proposed Rule, Federal Register, Vol. 61, No. 124. Pages 33259 - 33301.

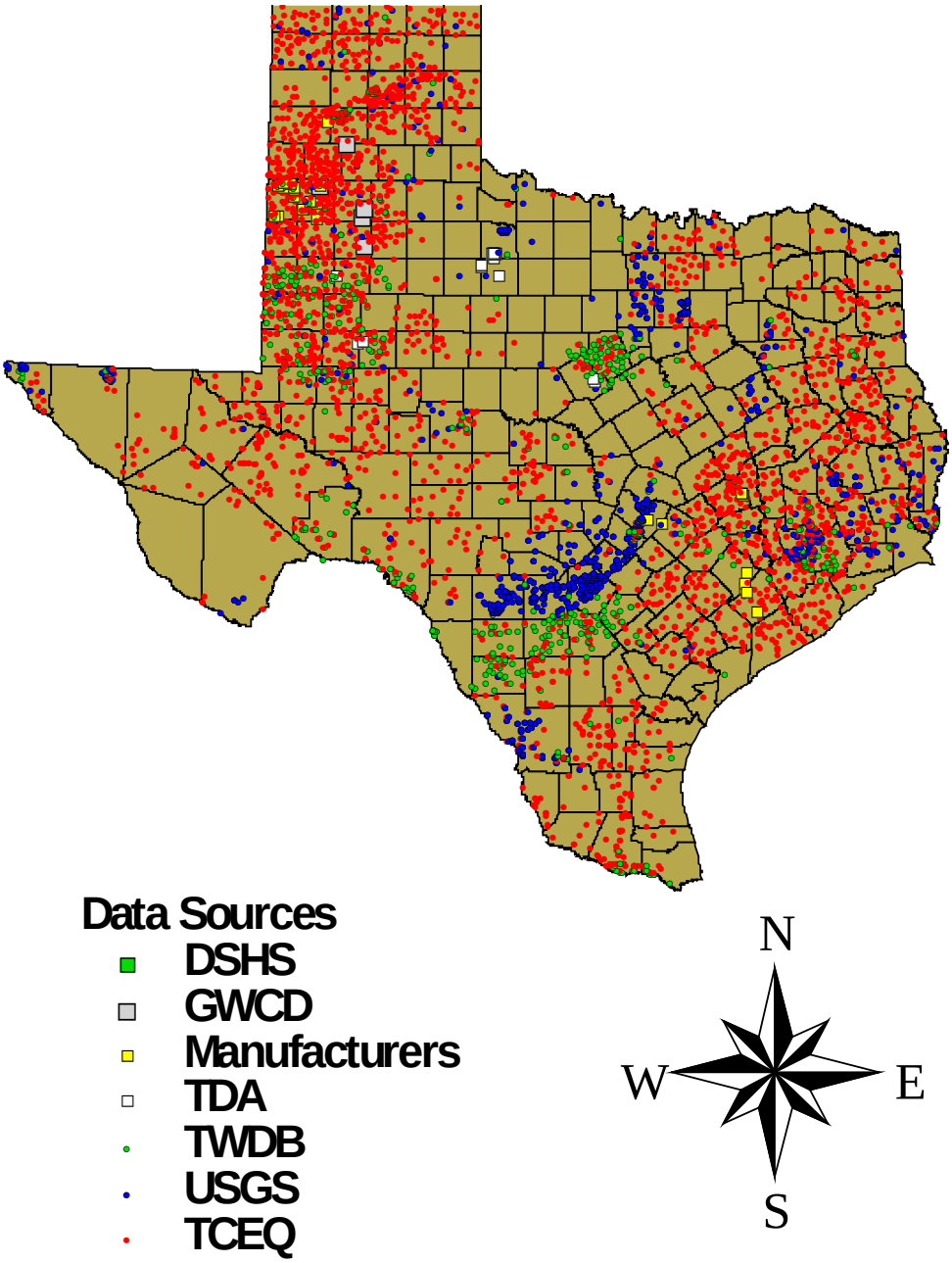
8. TNRCC, 2001(January), Texas State Management Plan for Prevention of Pesticide Contamination of Groundwater, Agricultural Chemicals Subcommittee of the Texas Groundwater Protection Committee, TNRCC SFR-070/01. 78 Pages.

9. Gilliom, Robert J., et. al.,2006, Pesticides in the Nation's Streams and Ground Water, 1992-2001, USGS Circular 1291. 180 Pages.

APPENDIX

IPD Data Sources

Figure 1



Appendix

Figure 2

Table 11: Analytical Results Table Structure

Field Number		Field Name	Type	Size	Key
1		Analyte	A	176	
2		Short Name	A	65	
3		USGS Parameter	A	6	
4		EPA Parameter	A	6	
5		Storet Code	A	6	
6		LessThan	A	3	
7		PQL or DL	N		
8		Concentration (ppb)	N		
9		Conc. Note	A	70	
10		Count as Detect?	A	1	
11		QA/QC	A	1	
12		Pass QA/QC?	A	1	
13		Notes	M	8	
14		Sample Relate	A	40	■
15		Well Relate	A	20	■
16		State Well No	A	7	
17		Sample No	A	35	
18		Data Origin	A	25	

Appendix

Figure 3

Table 12: Sampling Event Information Table Structure

Field Number		Field Name	Type	Size	Key
1		Sample Relate	A	40	■
2		Duplicate	A	6	
3		Duplicate of	A	40	
4		Resampling	A	11	
5		Sample No	A	35	
6		Other No	A	30	
7		Composite No	A	8	
8		Medium	A	20	
9		Test Method	A	50	
10		Hold-Time	N		
11		Date Sampled	D		
12		Time Sampled	A	6	
13		Sampling Agency	A	35	
14		Data Origin	A	25	
15		Data Source	A	35	
16		Long Project Description	A	60	
17		General Program	A	35	
18		Lab Split	A	1	
19		Lab	A	40	
20		Notes_1	M	8	
21		Well Relate	A	20	■
22		State Well No	A	7	

Appendix

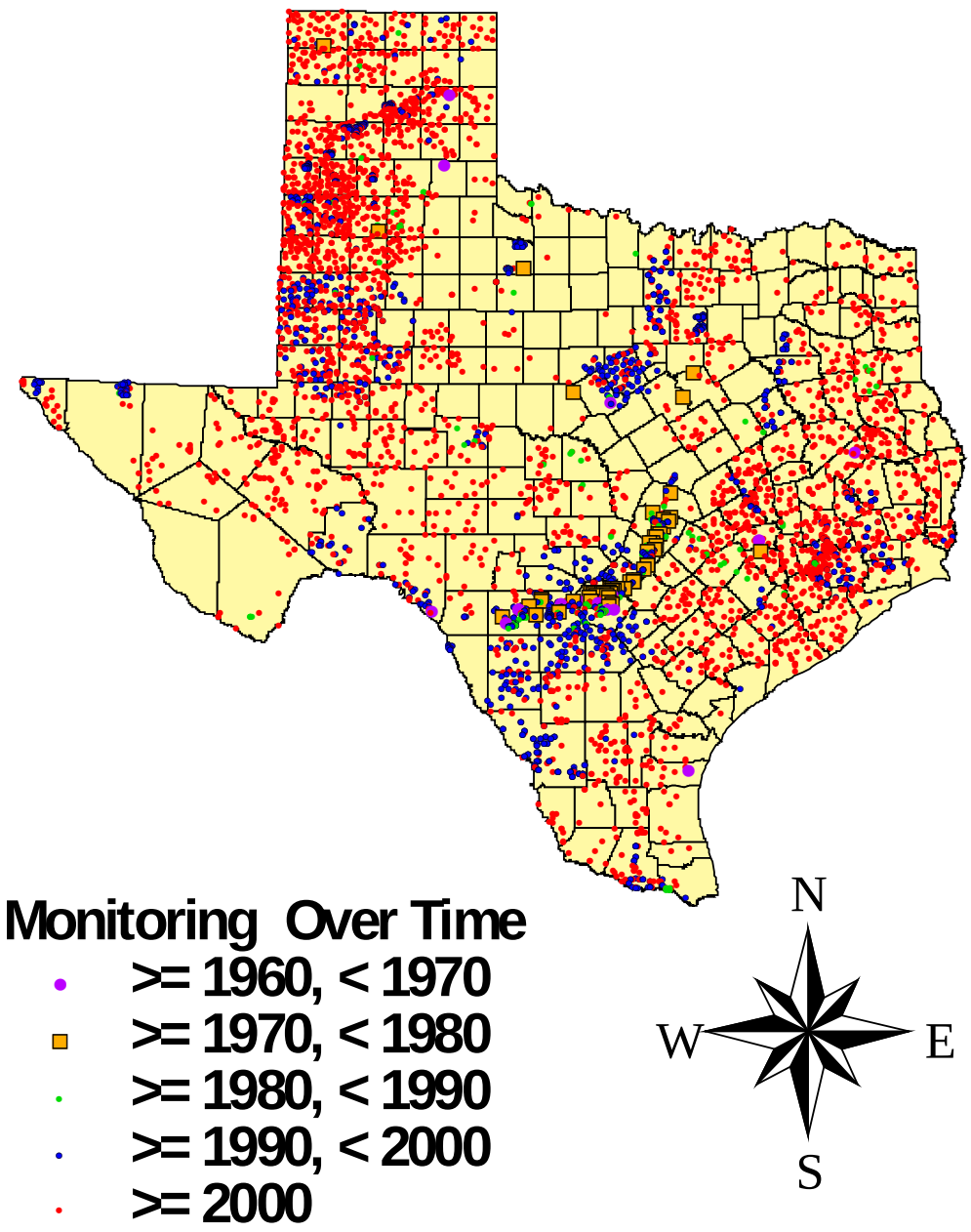
Figure 4

Table 13: Well Information Table Structure

Field Number		Field Name	Type	Size	Key
1		Well Relate	A	20	■
2		State_well_number	I		
3		State Well No	A	7	
4		Other Number	A	25	
5		Other Well No	A	25	
6		Site Type	A	15	
7		Latitude	A	13	
8		Longitude	A	13	
9		DECLAT	N		
10		DECLONG	N		
11		Owner	A	50	
12		Address1	A	21	
13		City	A	12	
14		State	A	2	
15		Zip	A	5	
16		Zip+4	A	4	
17		Phone	A	13	
18		Well No_1	A	14	
19		Co (FIPS)	S		
20		County	A	14	
21		Basin	A	4	
22		Aquifer	A	17	
23		Elevation	A	8	
24		T Depth	A	8	
25		Compl Date	D		
26		Completion Date	A	10	
27		Casing Dia (in)	S		
28		Well Type	A	1	
29		Well Use	A	18	
30		Reporting Agency	A	2	
31		Notes	M	8	

Monitoring Activity Over Time

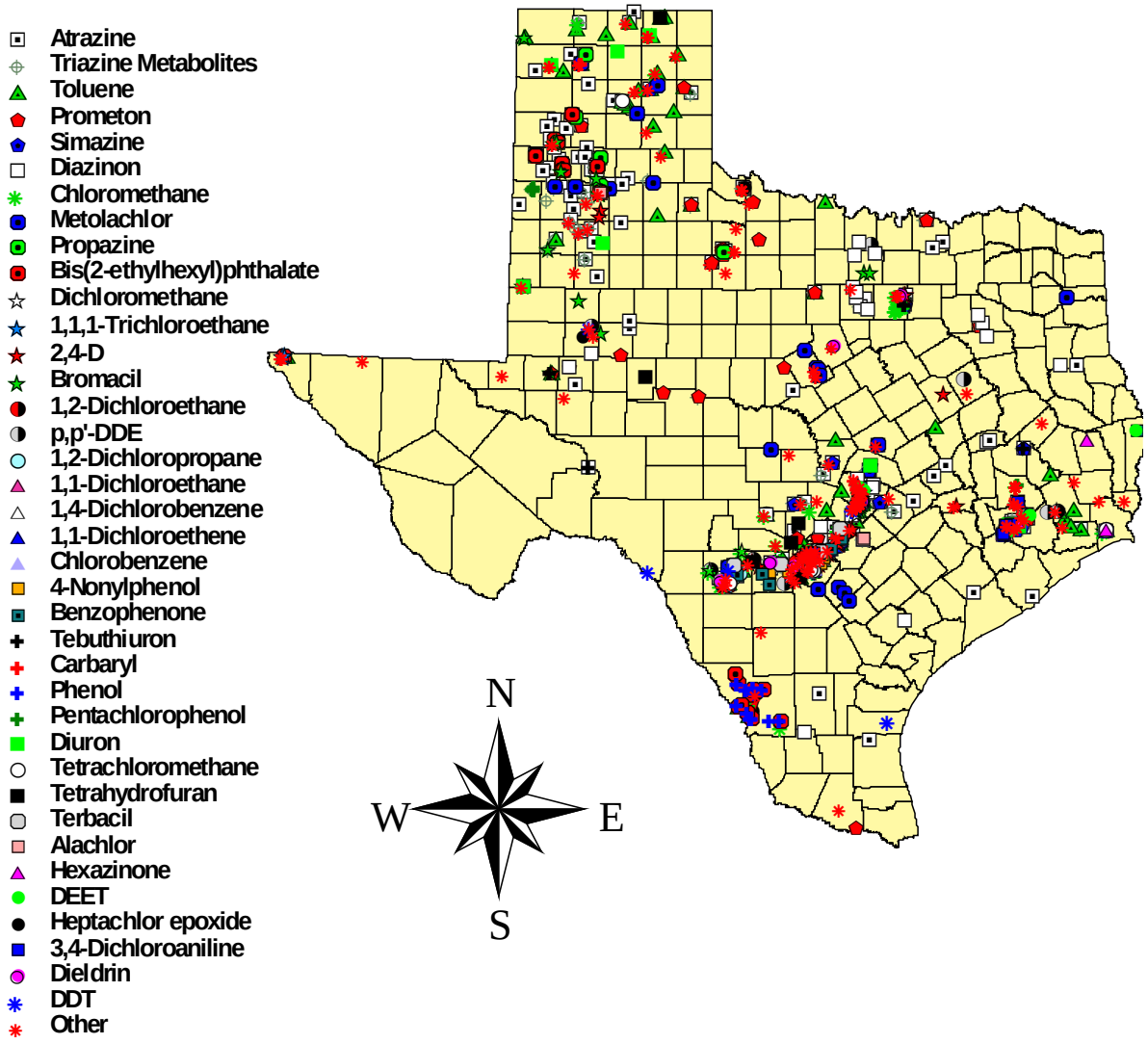
Figure 5



All Detections by Pesticide

(Only pesticides shown that have six or more detections.)

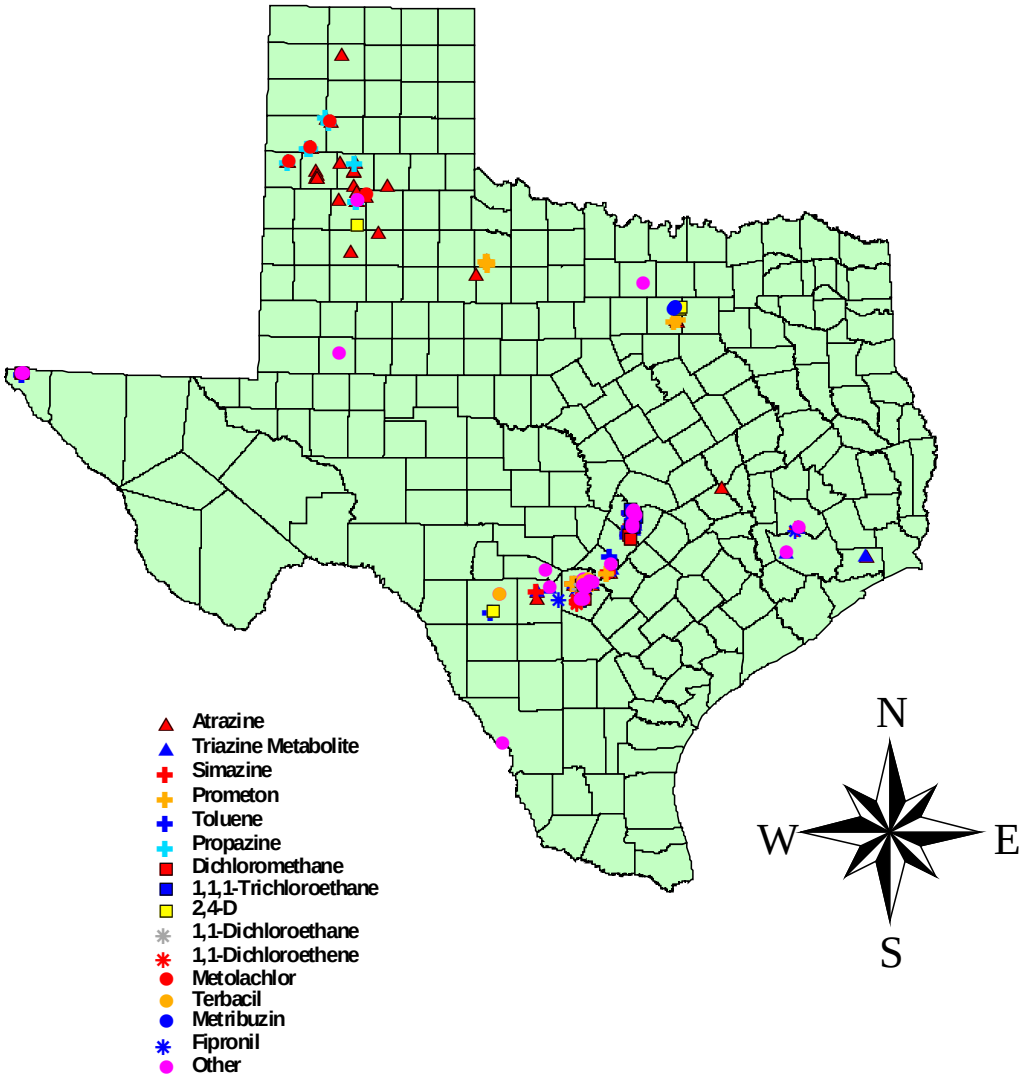
Figure 6



Confirmed Detections

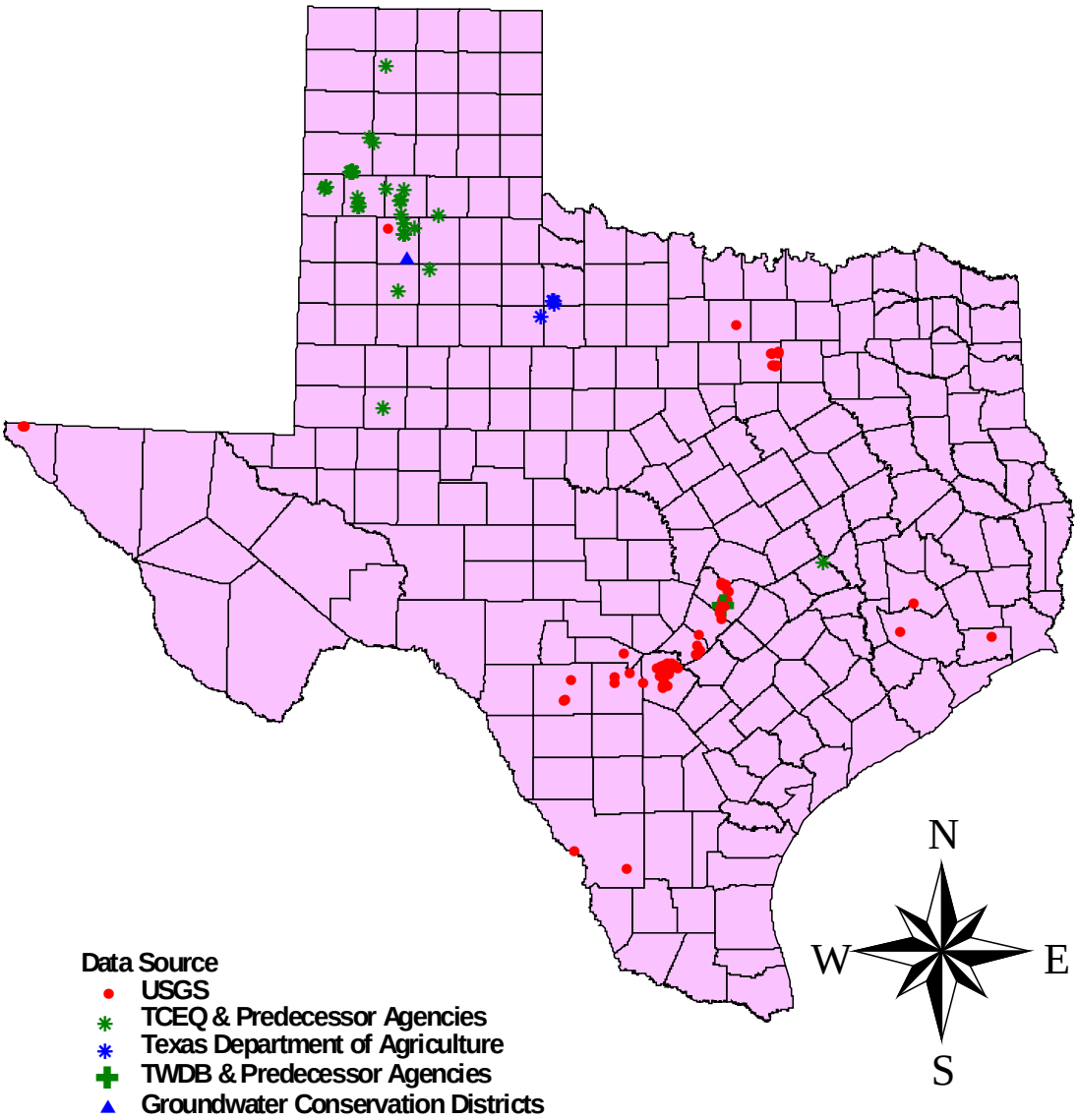
(Only pesticides shown that have three or more confirmed detections.)

Figure 7



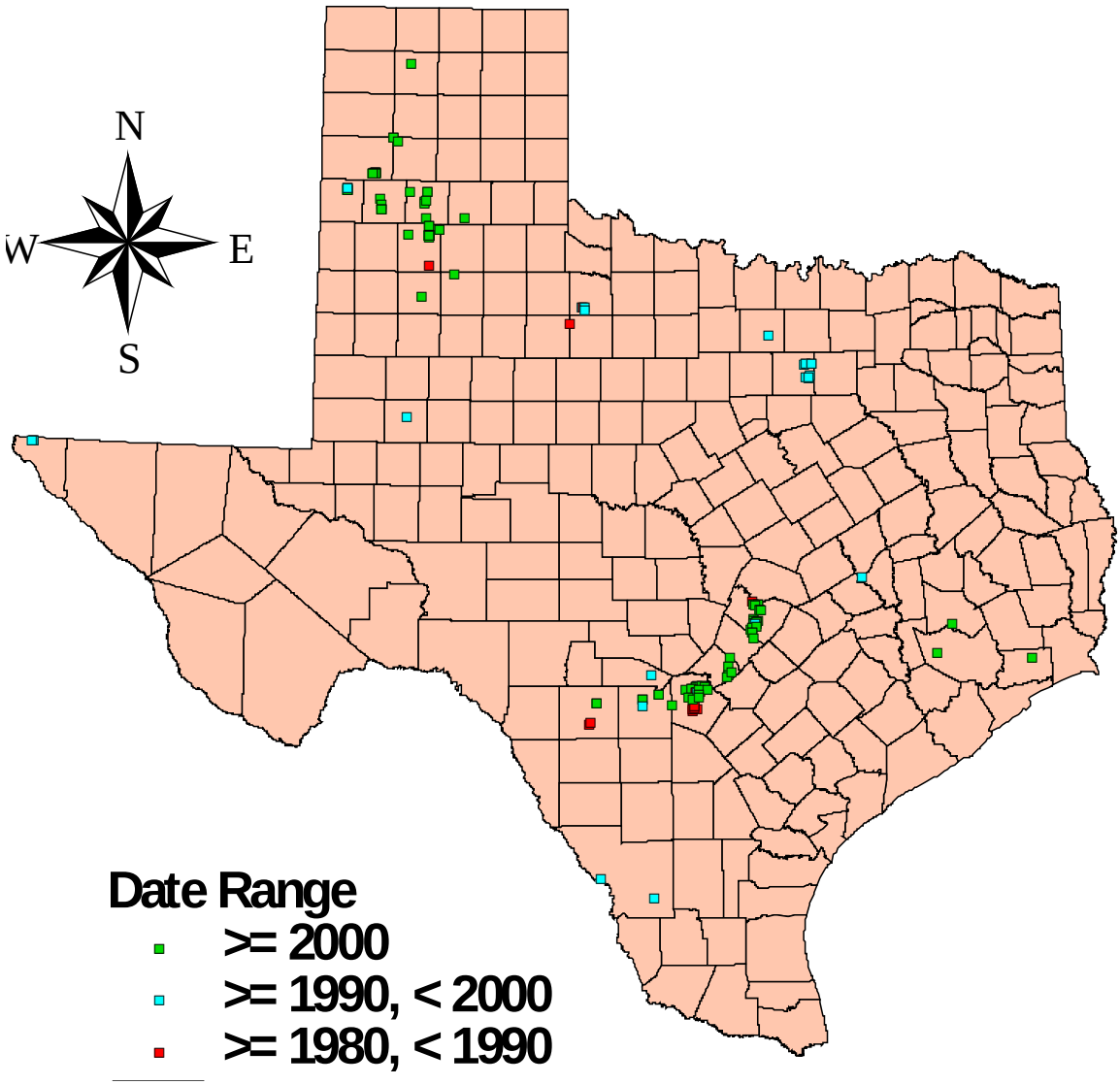
Confirmed Detections by Data Source

Figure 8

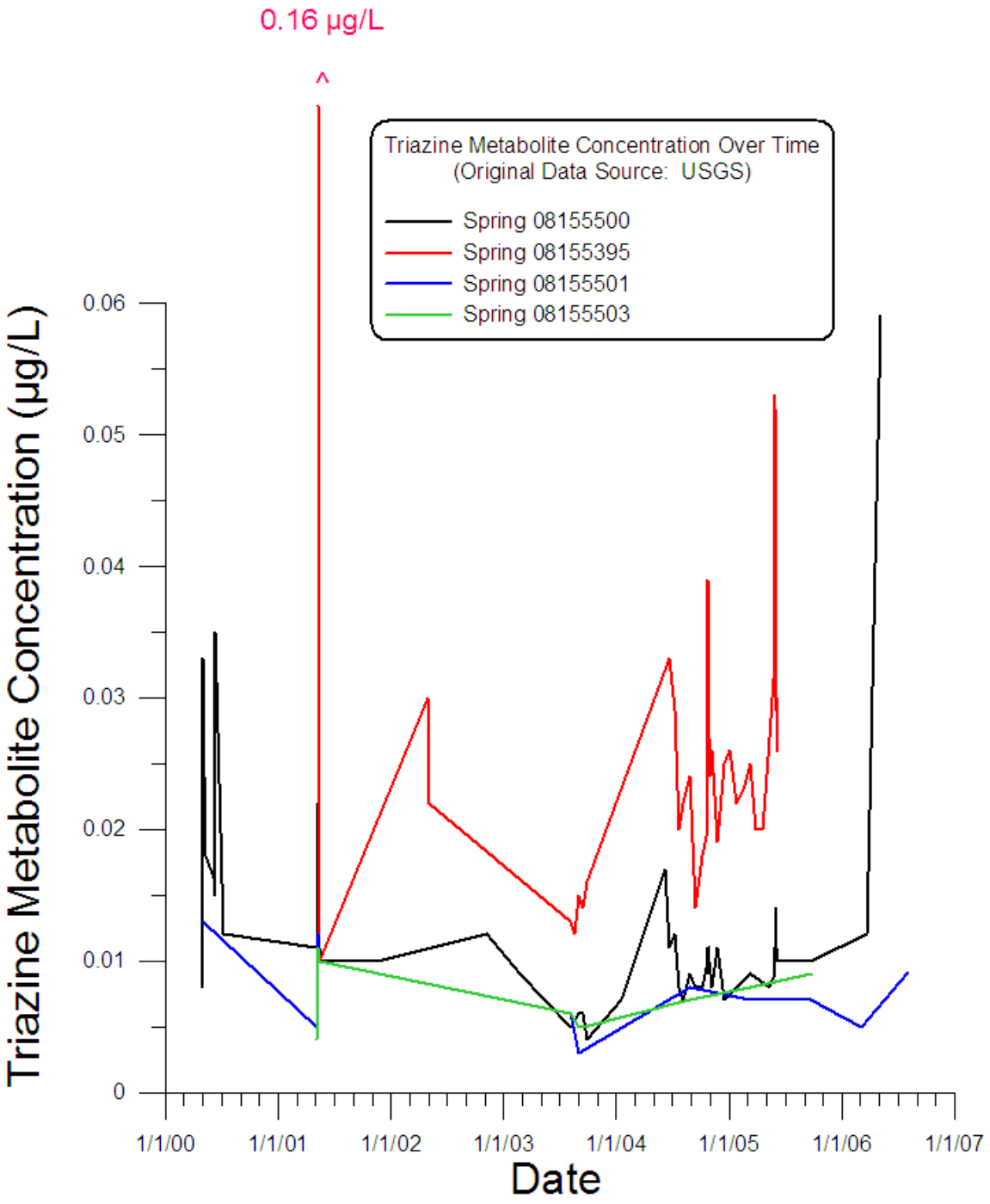


Confirmed Detections Over Time

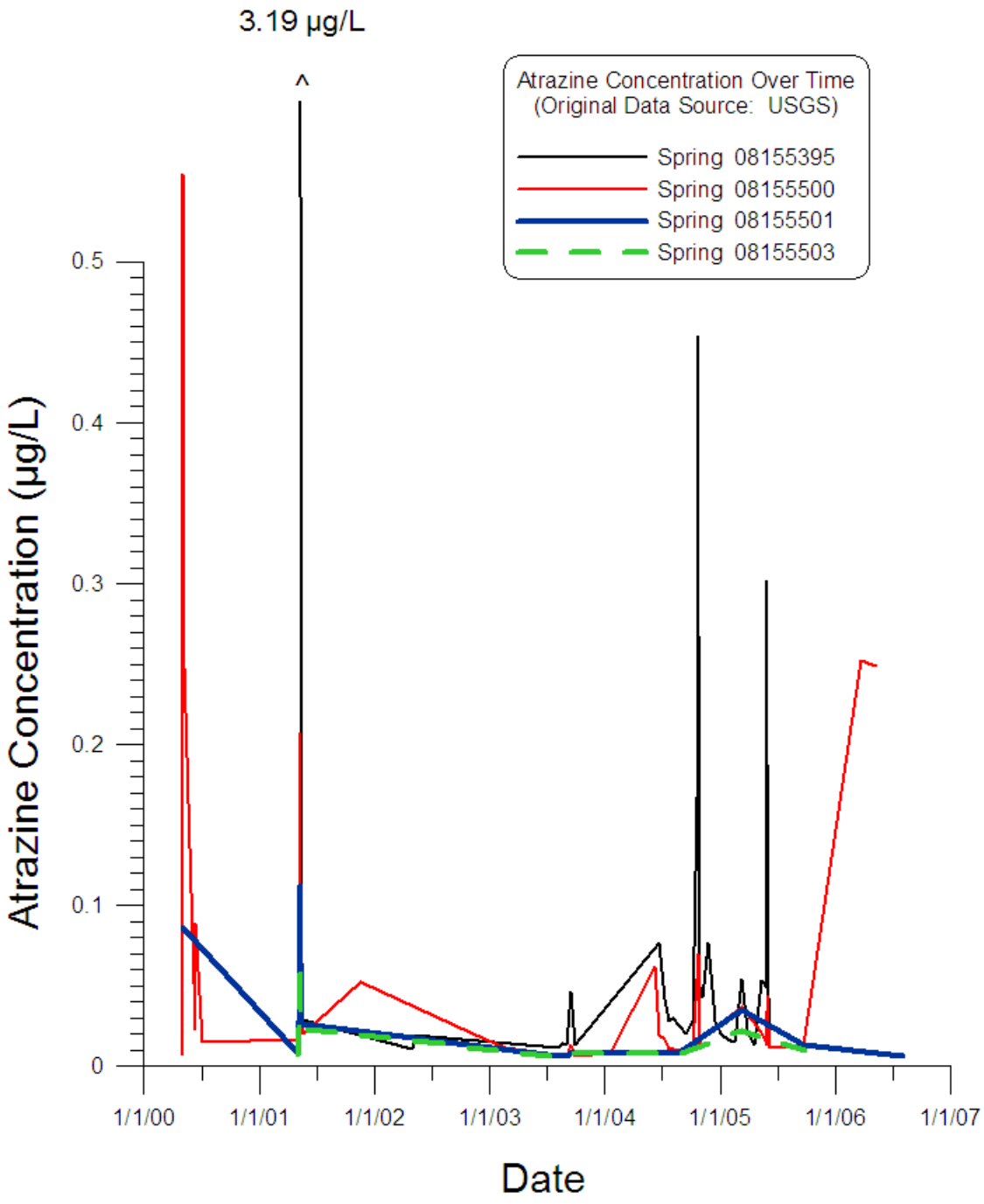
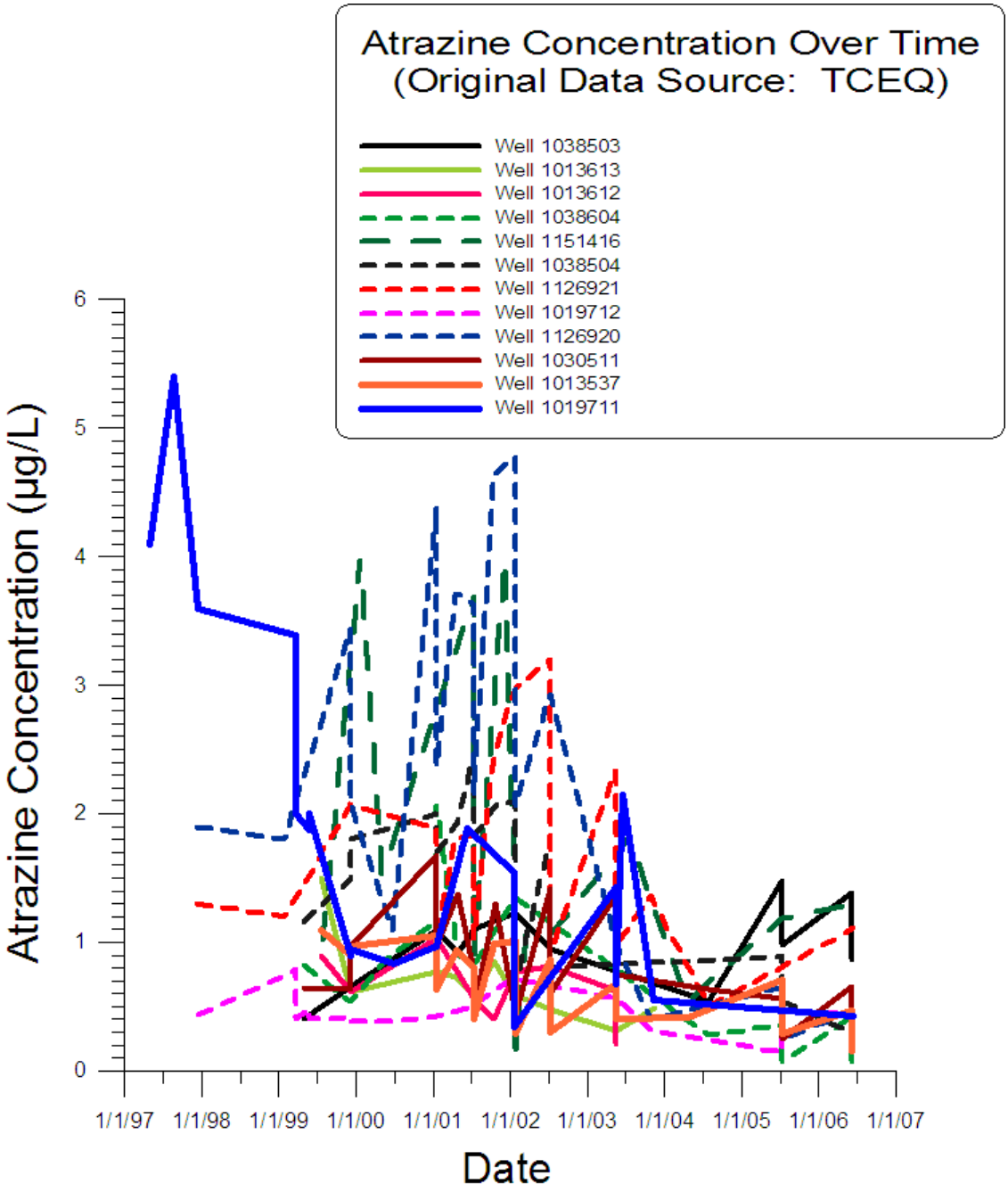
Figure 9



Triazine Metabolite Concentration Over Time
(2-Chloro-4-isopropylamino-6-amino-s-triazine)
Figure 10



Atrazine Concentration Over Time
Figure 11



Atrazine Concentration Over Time
Figure 12