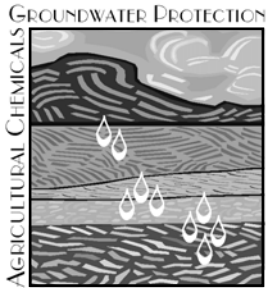
2007 ANNUAL REPORT

THE AGRICULTURAL CHEMICALS AND GROUNDWATER PROTECTION ACT

Colorado Department of Agriculture
Colorado State University Extension
Colorado Department of Public Health and Environment



www.ag.state.co.us/CSD/GroundWater/Waterhome.html

Colorado Department of Agriculture
Colorado State University Extension
Colorado Department of Public Health and Environment

Executive Summary

Colorado Department of Agriculture (CDA)

Storage Rules

Section 25-8-205.5 (3)(b) of the Agricultural Chemicals and Groundwater Protection Act requires the Commissioner of Agriculture to develop rules where pesticides and fertilizers are stored or handled in quantities that exceed the established thresholds. Pesticide and fertilizer facility inspections continued in 2007.

Federal Regulations for Pesticide Containment

The EPA's final regulations, *Standards for Pesticide Containers and Containment*, were published on August 16, 2006 (Federal Register Vol. 71, Number 158, pp. 47329 – 47437). Colorado (CDA) submitted its request to continue implementing its rules in lieu of the Federal regulations in August 2007, and is currently waiting on guidance from EPA on how to proceed with its justification for complying with the federal regulations.

Pesticide Use Survey

The CDA and CSUE conducted an on-line pesticide use survey for Colorado in 2007. Over 900 licensed, commercial pesticide applicators in Colorado's 64 counties were asked to participate in this voluntary, anonymous survey. After collecting information on types of pesticides applied and use patterns by the commercial applicators, a

report will be developed that will present the findings and be made available to interested parties.

Long Term Monitoring Plan

In 2007, Program personnel completed a long-term monitoring plan for the Program (*Long-Term Groundwater Monitoring Strategy and Plan*). This document will be used to drive program monitoring efforts for the next 5-10 years and will also help determine where new well networks should be installed.

Groundwater Quality Database Project

In 2007, Program personnel, in conjunction with the Integrated Decision Support Group in the Civil Engineering Department at CSU, completed a publically available, web-based tool that will interactively query the groundwater quality information associated with the Program.

Surface Water Sampling Project

The CDA is working with the CDPHE and EPA to coordinate a surface water sampling program to help satisfy CDA's responsibility for an EPA requirement that states evaluate a list of *Pesticides of Interest*.

Advisory Committee

The Advisory Committee continues to be an integral part of the implementation of this program by providing input from the many facets of the agricultural community and the general public that they represent (Appendix V). The committee met once during 2007.

Groundwater Monitoring

In 2007, the Groundwater Protection Program completed the 13th year of a long-term monitoring effort on the section of the South Platte River running from Brighton to Greeley, in Weld County. Between June and September 2007, 28 irrigation wells, 17 monitoring wells and 10 domestic wells were sampled. Three monitoring wells that were previously damaged or dry were reinstalled in winter 2007 and three new monitoring sites were established. Nitrogen analysis at the CDA laboratory determined that mean and median nitrate concentrations

were below historical values and the percentage of wells exceeding the EPA drinking water standard was lower than historical values for all three networks. There were a total of seven pesticide detections from all three networks, but only 10 of the 28 irrigation wells sampled underwent pesticide analysis. The monitoring well network had one detection for metalaxyl in one well, while the irrigation network had one detection each of phosphamidon and oxydemeton-methyl and two detections of dichlorvos. One domestic well detected dimethoate and another detected diazoxon, the breakdown product of diazinon. This year marked the first time in which there were no detections of any of the top four most commonly detected pesticides in Weld County (atrazine, desethyl atrazine, metolachlor, and prometon). Changes from what had been used historically for sampling methodology, sample preservation technique, and laboratory methods, may have affected pesticide results; however, the Program plans to thoroughly evaluate these factors during the 2008 field season.

The Front Range Urban Monitoring Network was expanded in 2007 to more thoroughly cover urban areas along the Front Range. Cooperation occurred with city governments, school districts, and private and federal entities. The Program was able to install monitoring wells in Fort Collins and Colorado Springs, in addition to obtaining permission to use existing wells in Denver-metro, Castle Rock, Pueblo, and Greeley. In total, the network now has almost 80 sites with plans to establish 5-10 sites in Boulder and possibly 3-6 more sites in Colorado Springs in 2008. All locations will be sampled during the 2008 field season and will have baseline analysis for 104 pesticides, basic inorganic nutrients, and dissolved metals.

The San Luis Valley was sampled in August and September, 2007, through cooperation with the Unites States Geologic Survey (USGS). Thirty-three wells were sampled in total with 21 of the wells being wells that were reinstalled deeper into the unconfined aquifer due to a declining water table. Results from the reinstalled wells are being treated as a new sample population and 2007 data for the wells will determine a new baseline. Ten of twelve other wells not reinstalled, and which were sampled in both 2000 and 2007, did not show much evidence of decreasing nitrate concentrations in the aquifer, even though the median for these wells decreased by nearly 78%. Mapped

nitrate results from all wells, independent of well depth, does not show a significant decrease in the number of wells with nitrate above 10.0 ppm from 2000 to 2007; however, there were four wells below the detection limit in 2007 versus two in 2000. Preliminary pesticide results from the USGS laboratory show a total of 22 pesticide detections in 15 of the 33 sampled wells with the most commonly detected pesticides being metribuzin and metolachlor.

Colorado State University Extension (CSUE)

Summary of Accomplishments

Conducted educational programs throughout Colorado on issues related to agricultural chemicals and groundwater quality. Groups addressed include: crop and livestock producers, commercial applicators, chemical dealers, conservation districts, crop consultants, NRCS agency personnel, homeowners, private well owners, real estate professionals, and urban chemical users.

Worked to coordinate efforts of the Agricultural Chemicals and Groundwater Protection program with other state and federal programs in Colorado.

Conducted training related to the Colorado Best Management Practices Manual. Distributed publications to Colorado citizens covering nutrient, pesticide, irrigation, manure, corn, pesticide record keeping, and private water well management.

Conducted a second year of field demonstration and applied research on limited irrigation under three plant populations for grain corn and limited irrigation of wheat following onions.

Established a new on-farm site near Greeley to demonstrate cover crops as a transition to dryland or permanent grass for land that lost irrigation water.

Conducted irrigation management demonstrations on farmer fields in the Arkansas Valley. Demonstrations included: using crop water use (ET) from the CoAgMet weather stations network and WaterMark® soil moistures for improved irrigation scheduling.

Helped CDA establish a new dedicated urban well monitoring network, primarily through communication with cooperating municipalities and other public entities.

Conducted nitrogen management applied research and demonstrations on farmer fields near Prospect Valley, Colorado for the third year, using the pre-sidedress soil nitrate test (PSNT) for corn when applied with poultry manure in cooperation with Parker Ag Services Company.

Continued to cooperate with the Colorado Climate Center to promote and improve the crop water use (ET) reports provided by the Colorado Agricultural Meteorological Network (CoAgMet). See www.CoAgMet.com.

Served on the Colorado board for the Certified Crop Advisors Program as exam chair responsible for conducting the state exam.

Maintained a CSU Extension Water Quality Website to disseminate BMP information via the Internet (www.csuwater.info).

Distributed revised series of four fact sheets on the web to educate Colorado homeowners on BMPs for urban pesticide and fertilizer use.

Revised, reprinted, and distributed the Irrigated Field Record Book.

Updated the Microsoft Excel® and .pdf versions of the Pesticide Record books for Private Applicators and made these products available for download at www.csuwater.info.

Worked with CDA to finish the development of a web-interactive database utilizing the Integrated Decision Support (IDS) Group at CSU to present the Program's groundwater quality data to the general public and other agencies. See:
http://wsprod.colostate.edu/cwis435/WQ/index.html

Served on the planning committee for the 2007 South Platte Forum. The SP Forum is an interdisciplinary conference that brings together

diverse interests in water to communicate and get the latest on water quantity and quality science and policy in the basin.

Colorado Department of Public Health and Environment (CDPHE)

During 2007, the Colorado Department of Public Health and Environment continued to be actively involved with the Agricultural Chemicals and Groundwater Protection Program. The CDPHE continues to review the Program's monitoring data on an annual basis, and provide input on the results. Other activities that the Department has assisted the Program with include work on the Program's Long Term Monitoring Plan and Groundwater Quality Database Project.

2007 Annual Report
Colorado Department of Agriculture

Rules for Agricultural Chemical Bulk Storage Facilities and Mixing/Loading Areas

Section 25-8-205.5 (3)(b) of the Agricultural Chemicals and Groundwater Protection Act requires the Commissioner of Agriculture to develop rules where pesticides and fertilizers are stored or handled in quantities that exceed the established thresholds. These rules were adopted in July 1994 and became effective September 30, 1994.

During 2007, facilities were visited to provide information and answer specific questions regarding the rules for bulk storage and mixing/loading facilities. This educational process aids individuals in determining first, whether or not compliance with the rules is required and second, what specifically must be accomplished to meet the requirements.

Pesticide and fertilizer facility inspections continued in 2007. A total of nine pesticide secondary containment structures and 16 pesticide mixing/loading areas were inspected. A total of 21 fertilizer secondary containment structures and 21 fertilizer mixing/loading areas were also inspected. A total of 35 follow-up inspections were also conducted to ensure that problems noted on previous facility inspections were corrected. In addition, five Violation Notices and three Cease and Desist orders were issued during 2007. Finally, 20 follow-up inspection orders were issued for problems at facilities that were not serious enough at this time to warrant a Cease and Desist Order or Violation Notice. Inspection of pesticide and fertilizer facilities will be ongoing during 2008.

One requirement of the rules is that the facility design be signed and sealed by an engineer registered in the state of Colorado; or the design be from a source approved by the Commissioner and available for public use. The Colorado Department of Agriculture (CDA) in conjunction with Colorado State University Extension (CSUE) produced a set of plans that meet the second criteria. The document is entitled, *Plans For Small To Medium-Sized Agricultural Chemical Bulk Storage & Mix/Load Facilities.* The plans are available from CDA or CSUE free of charge.

Copies of the complete rules and a summary sheet that contains a checklist to allow individuals to determine if the rules apply to their operation are also available from CDA, CSUE, or via CDA's website at *www.colorado.gov/ag.*

Pesticide Registration and Groundwater Protection

The Program continues to review pesticide products for registration in Colorado which have groundwater label advisories, and advise CDA's Pesticide Registration Program on the merits of registering these products.

Federal Regulations for Pesticide Containment

The Environmental Protection Agency (EPA) proposed standards for pesticide containers and containment in 1994 and has taken public comment three times, in 1994, 1999, and again in 2004. The EPA's final regulations, *Standards for Pesticide Containers and Containment* (Federal Register Vol. 71, Number 158, pp. 47329 – 47437), were published on August 16, 2006. The EPA will allow states with existing pesticide containment rules to continue implementing the State's rules if EPA determines that these rules are equivalent in environmental protection to EPA's new regulations. Colorado (CDA) submitted its request to continue implementing its rules in lieu of the Federal regulations in August 2007, and is currently waiting on guidance from EPA on how to proceed with its justification for complying with the federal regulations.

Waste Pesticide Disposal

In 1995, CSUE operated a pilot waste pesticide collection program in Adams, Larimer, Boulder, and Weld counties. The purpose of this type of program is to provide pesticide users an opportunity to dispose of banned, canceled, or unwanted pesticides in an economical and environmentally sound manner. Part of the funding for the program was provided by an EPA Nonpoint Source 319 grant. Approximately 17,000 lbs. of waste pesticides from 67 participants was collected and safely disposed.

Based on the success of this pilot program, CDA was asked to continue a program that could collect and dispose of waste pesticides in other areas of the state. However, CDA had no statutory authority or funding to operate such a program. In light of this, two alternatives were discussed as a way for a waste pesticide collection program to continue. The first was for CDA to seek statutory authority and funding from the Legislature to operate a state-run program. The second was

to determine if a private program, operated by a hazardous waste handling company, was possible.

The CDA spoke with hazardous waste contractors to determine if they would be interested in attempting to collect and dispose of waste pesticides as a private program. One company, MSE Environmental Inc., stated they would be interested. Discussions were initiated with the company and it appeared it would be possible for MSE to operate a private program at a reasonable cost to the participants. The collection and disposal costs for participants would be between $2.25 and $2.65 a pound.

Based on this information, it was determined that the private program option would be pursued since the possibility of getting legislation passed was slim. Furthermore, the time required for legislation to be passed would considerably delay the operation of a program. After numerous issues were addressed, MSE targeted two areas of the state to initiate the program - the San Luis Valley and six counties in northeastern Colorado. This program was very successful with over 10,500 lbs. of waste pesticides collected from 33 participants; the cost to participants was $2.65 per pound.

Based on the success of this program, MSE conducted a statewide collection program in November 1997. Over 23,000 lbs. of waste pesticides were collected from 75 participants; again the cost was $2.65 per pound. Subsequent programs are as follows:

Year	Pesticides Collected (lbs.)	Number of Participants
1998	0	0
1999	19,792	47
2000	0	0
2001	13,486	34
2002	8,762	33
2003	2,254	7

2004	8,520	10
2005	5,023	11
2006	No Report	No Report
2007	No Report	No Report

In 2006, Clean Harbors, Inc. took responsibility for this program from MSE. The CDA is working with Clean Harbors to make sure this program continues in an efficient manner.

Pesticide Use Survey

The CDA and CSUE conducted an on-line pesticide use survey for Colorado in 2006 and 2007. Due to an inadequate response in 2006, the survey was conducted again in 2007. The last pesticide use survey was done in 1997 and, after 10 years, updated information is needed. This information is particularly important to help the Department register pesticides for use, especially Section 18 requests, update crop profiles, and provide correct data to keep products registered under the Food Quality Protection Act (FQPA). It also helps provide unbiased, accurate information to identify and address environmental concerns and to focus CDA's water quality monitoring efforts. Updated information is also necessary to better focus the Department's resources on areas that have the greatest potential to impact public health and the environment.

There are over 900 licensed, commercial pesticide applicators in Colorado's 64 counties that will be asked to participate in this voluntary, anonymous survey. After collecting information on types of pesticides applied and use patterns by the commercial applicators, a report will be developed that will present the findings and be made available to interested parties.

Program Comprehensive Publication

In 2007, Program personnel continued working on a comprehensive publication that will provide a history of the work and accomplishments of the Program since 1990. This is an ongoing project that has parts from CDA, CSUE, and CDPHE. The projected publication date is spring of 2008.

Long Term Monitoring Plan

In 2007, Program personnel completed a long-term monitoring plan for the Program (*Long-Term Groundwater Monitoring Strategy and Plan*). This document will be used to drive program monitoring efforts for the next 5-10 years and will also help determine where new well networks should be installed.

Groundwater Quality Database Project

In 2007, Program personnel, in conjunction with the Integrated Decision Support Group in the Civil Engineering Department at CSU, completed a publically available, web-based tool that will interactively query the groundwater quality information associated with the Program. Since 1992, over 4,600 samples from approximately 935 wells have been collected throughout Colorado. The website contains information on all water quality constituents collected by the Program including pesticides, nitrate-nitrogen, and inorganic constituents. The data is searchable by an array of parameters, such as water quality constituent, geographic location, and year detected. An ARC- IMS map is also available to interactively search the database.

Surface Water Sampling Project

The EPA may require CDA to begin collecting surface water samples for pesticides based on the recent *Pesticides of Interest* list EPA has created. The CDA is responsible for reporting on how it is managing the approximately 50 pesticides on this list that may affect ground and/or surface water. The CDA is working with the CDA, CDPHE, and EPA laboratories to coordinate how samples will be analyzed. The CDA is also coordinating with CDPHE to collect split samples from the surface water samples CDPHE currently collects each year. The plan for 2008 is to analyze about 20 samples and then evaluate the process before committing more resources to this project. From CDA's perspective, it will be interesting to see how surface water is being impacted by pesticides and how this might relate to CDA's groundwater sampling program for pesticides.

Groundwater Monitoring

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below historical values and the percentage of wells exceeding the EPA drinking water standard was lower than historical values for all three networks. There was a total of seven pesticide detections from all three networks, but only 10 of the 28 irrigation wells sampled underwent pesticide analysis. The monitoring well network had one detection for metalaxyl in one well, while the irrigation network had one detection each of phosphamidon and oxydemeton-methyl and two detections of dichlorvos. One domestic well detected dimethoate and another detected diazoxon, the breakdown product of diazinon. This year marked the first time in which there were no detections of any of the top four most commonly detected pesticides in Weld County (atrazine, desethyl atrazine, metolachlor, and prometon). Changes from what had been used historically for sampling methodology, sample preservation technique, and laboratory methods, may have affected pesticide results; however, the Program plans to thoroughly evaluate these factors during the 2008 field season.

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sampled wells with the most commonly detected pesticides being metribuzin and metolachlor.

Weld County Long Term Project

History

Analysis of groundwater samples, in 1995, resulted in the discovery of elevated levels of nitrate in the South Platte River alluvial aquifer. The Program was interested in developing a long-term monitoring effort on the Brighton to Greeley stretch of the South Platte River which lies inside the Weld County boundary. The Weld Long Term Network is composed of three different network types: a) Twenty dedicated monitoring wells permitted by the Central Colorado Water Conservancy District; b) Fifty-five irrigation wells sampled continuously since 1994; and c) Ten domestic wells first sampled back in 1992. Irrigation and monitoring networks are sampled annually, while sampling of the domestic network only occurs once every three years with 2004 being the most recent sampling. Irrigation, domestic, and monitoring well samples all undergo analysis for nitrate and nitrite, but the monitoring well samples were screened for suite of 47 pesticides. Prior to 2005 the irrigation and domestic well samples underwent pesticide analysis for triazine herbicides through use of an immuno-assay; however, due to the manufacturer's discontinuation of this testing kit, triazine analysis on these wells was not conducted in 2005 or 2006.

The Program's Weld Long Term project has, as of 2006, collected 924 groundwater samples with irrigation, monitoring, and domestic wells comprising 68.5, 24.4, and 7.1% of all samples, respectively. Long term data from 1995-2006, shows that 72.8 and 70.2% of all irrigation and monitoring well samples, respectively, have had nitrate concentrations above the EPA drinking water standard of 10.0 ppm. In 2006, these percentages were 79.5 and 76.5% respectively, suggesting a higher than average number of samples with nitrate greater than 10.0 ppm; however, all statistical values with regards to nitrate concentration in 2006 are lower than historical values (Table 1).

Weld County Long-Term Nitrate Results							
	Sample #[a]	Mean	Median	Min	Max	Q1	Q3
Irrigation Wells							
1995-2005	575	17.35	16.40	0.24	81.98	9.70	24.16
2006	43	15.83	15.43	0.31	37.77	10.82	21.44
Monitoring Wells							
1995-2005	205	23.30	20.22	1.9	111.32	8.21	31.00
2006	19	19.28	15.47	3.3	72.73	7.44	24.35
a Only samples with a detectable quantity of nitrate are counted							

Table 1. Nitrate data from irrigation and monitoring well networks in the Weld County Long-Term project sampled from 1995 to 2006. Q1 and Q3 are the first and third quartiles. All values are in units of parts per million (ppm) except Sample #.

Review of historical pesticide detections shows that 19 different pesticide compounds have accumulated 852 detections in samples collected from Weld County Long Term well networks from 1995-2006. Due to this project's frequency of sampling, as opposed to others projects in the state, Weld County pesticide detections have accounted for 87.2% of the 977 total pesticide detections found to date, statewide. Irrigation and monitoring wells, sampled annually, have contributed 80.9%, or 790 detections, to that total.

The most commonly detected pesticides in Weld County are atrazine and its breakdown product desethyl atrazine (DEA), metolachlor, and prometon with 148, 118, 73, and 38 total detections, respectively. Monitoring wells alone have accounted for 47, 72, 74, and 100 %, respectively, of total detections of these four pesticides. Irrigation wells had 400 detections of triazines during the use of the immuno-assay kit from 1996 to 2004. The triazine family includes atrazine and desethyl atrazine. Domestic wells, sampled least frequently at once every three years, have substantially less influence on the total number of pesticide detections in the Weld County long-term project; however, atrazine and desethyl atrazine are still the most commonly detected pesticides in this network as well. Only twice has a pesticide detection been over EPA's maximum contaminant level (MCL); once in 1995 for a 0.9 ppb detection of Lindane (MCL = 0.6 ppb) in a domestic well, and again in 2001 for a 5.47 ppb detection of Atrazine (MCL = 3.0 ppb) in a monitoring well.

Network Sampling Frequency

For 2007, in addition to the monitoring wells, all domestic wells and a selection of 10 irrigations wells underwent analysis for pesticides. It was decided that the domestic well network will be sampled annually from now on in order to get the

needed data for long-term trend analysis. Furthermore, all future samples from irrigation wells will undergo complete pesticide analysis.

Laboratory Procedure Changes

In the past, a suite of 47 pesticide compounds were analyzed for the CDA. In May 2007, a new chemist was hired for the program. In depth details on procedures used in 2007 can be found in the Laboratory Update section of this report, but the following list summarizes some important changes with regards to pesticide analysis in 2007, which may or may not have affected 2007 results:

- In the future, all samples will be tracked with a Chain of Custody (COC) form
    - This assists in keeping sample information centralized
    - Confirms sample collection, delivery, and analysis within holding times
- The Pesticide Data Program (PDP) methodology for pesticide analysis was used in place of the method used by the program since 1995. This means:
    - New pesticides were analyzed for – 114 total parent compounds and breakdown products
    - Different chemicals were used for SPE extraction
- This change in methodology involved the use of a different standards calibration solution, and did not include the following pesticides which have been historically analyzed for by the program:
    - alachlor, acetochlor, bromacil, captan, DDT, heptachlor, lindane, MCPP, methoxychlor, metolachlor, and parathion
    - All these compounds, except captan, DDT, and 1-naphthol, will be added into the standards calibration solution for 2008 and all future analysis
- There was the adoption of more stringent criteria for determining the legitimacy of a detection and/or concentration of a pesticide.
    - This decreases the chance of a false positive but increases the time needed for evaluating the spectrographs
    - The large number of compounds being analyzed also increased the complexity in being able to get good peak separation between the various compounds which affects the accuracy of determining detections because of retention time interference.
- New sample preservation methods were adopted:
    - 1 L of sample is collected in an amber glass Boston round and has the following preservatives added:
        - L-Ascorbic Acid for dechlorination

        - EDTA to inhibit metal-catalyzed hydrolysis of target analytes
        - Diazolidinyl Urea as a microbial inhibitor
        - Tris(hydroxymethyl)aminomethane and Tris(hydroxymethyl)aminomethane hydrochloride as pH 7 buffers
    - 1 L of sample is collected in an amber glass Boston round and has sodium thiosulfate added as a preservative
- For 2008, the pesticide analyte list will be reviewed to determine which pesticides, out of the 112 analyzed for in 2007, should be retained for future analysis as not all PDP pesticides pose risk to groundwater contamination and several compounds are difficult to analyze.

Sampling Methodology Changes

In 2007, the program purchased a Geotech Geocontrol bladder pump system and a YSI 556-MPS multi-parameter probe with 500 mL flow-cell. The purchase of this equipment was to facilitate the adoption of a low-flow, minimum drawdown sampling method for sampling monitoring wells. The previous method used a Grundfos Redi-flo2 electric-drive pump and was based on the principle of evacuating three to five casing volumes of water from the well, before collecting a sample. Periodic samples were collected, during evacuation, so pH and electrical conductivity (EC), which are two parameters used to confirm when a well has been adequately purged, could be measured. This method has been used by the program for sampling monitoring wells since 1995 and has historically been the textbook way to sample monitoring wells throughout the scientific community. Current research and understanding however has determined that the criterion of purging 3-5 casing volumes may no longer the best purging method for all applications. Furthermore, the use of an electric-drive pump, which requires a high initial surge in order to establish a good flow, does not provide the most sound means of collecting an *in situ*, formation quality groundwater sample.

The main concept behind using a low-flow technique is to extract water from the well at a rate that is very close to or less than the recharge rate of the well. A draw-down meter is usually used to keep the maximum drawdown less than 0.33 ft during sampling and purging. Flow rates can therefore vary from site to site since the pumping rate is dependent on yield of the well (a product of aquifer transmissivity), but can include other factors. Typical flow rates range from 100 to 500 mL min^{-1} when using a low-flow sampling system. With such a low flow, compared to flow rates of 4 to 19 L min^{-1} using an electric-drive pump, there is an increase in the likelihood that water is being pulled from the well without

disturbing sediment and with less aggression. This adds insurance that an *in situ* sample is being collected from a discreet location in the aquifer.

The other facet of low-flow sampling is the incorporation of an in-line 500 mL flow-cell and multi-parameter probe. This allows that groundwater is measured for temperature, EC, DO, pH, and oxidation-reduction potential (ORP) without coming into contact with atmosphere. The measurement frequency varies from site to site and is dependent on the flow rate and flow-cell cycle period. Parameters are compared to the desired criteria in Table 4, which upon being met, declares the well adequately purged and ready for sampling. These criteria may be achieved prior to having pumped 3-5 casing volumes of water from the well, but it is assumed that formation quality water is being produced immediately upon stabilization.

Stabilization Criteria

		YSI 556-MPS	
Parameter	Desired	Accuracy	Range
pH	± 0.2	± 0.2 units	0 - 14 units
EC	± 5%	± 0.5% of reading or ± 0.001 mS/cm, whichever is greater	0 - 200 mS/cm
ORP	± 20 mV	± 20 mV	
DO	± 10%	**0-20 mg/L:** ± 2% of reading or 0.2 mg/L, whichever is greater	0 - 200 %
		20-50 mg/L: ± 6% of reading	200 - 500 %

Table 2. Stabilization criteria used to determine when a monitoring well is adequately purged and ready for sampling. A YSI 556-MPS multi-parameter probe is installed in a 500 mL flow-cell as part of a low-flow, minimum draw-down sampling methodology. Measurements are collected, once every flow-cell cycle, until parameters have stabilized to the desired criteria given the accuracy and range of the various probes.

Changing the method in which a groundwater sample is collected from monitoring wells could possibly impact the pesticide detection and/or concentration results. In 2008, the Program intends to collect samples from at least ten Weld County long-term monitoring wells using both sampling methods to determine if sampling methodology is influencing pesticide detections and/or concentrations. Nitrate variability will also be evaluated but differences are not expected. Past research efforts in the scientific community have concentrated primarily on volatile compounds when evaluating different sampling techniques. Nearly all pesticides analyzed by the Program are not volatile in nature and unfortunately research efforts by others have not specifically evaluated a large variety of pesticides. Therefore, it is necessary to conduct our own study to compare the low-flow

bladder pump, multi-parameter stabilization method to the electric-drive pump, and 3-5 casing volume method with respect to differences in detections and/or concentrations of 100+ pesticide compounds. The results will greatly dictate how 12 years of data collected with the Grundfos Redi-flo2 sampling equipment should be related to future results from samples collected with a low-flow bladder pump. It is the desire of the Program to properly design this study and conduct a literature review in order that the findings can be made available to, and accepted by, the scientific community.

Well Network Improvements

The monitoring well network had three wells which were either damaged or dry, and therefore had not been sampled for as far back as 1999. These wells were re-installed at the same location, but were drilled deep enough, if possible, to set a 10 ft section of 10-slot screened PVC-SCH40 pipe so that the top two feet of the pipe were above the current water table.

The Program was also granted permission from three landowners to install four new monitoring wells in fall 2007. One new location, about one mile north of Platteville, has two monitoring wells installed at different depths. The samples collected from these two wells will be useful in determining how the water chemistry differs with depth at this location in the South Platte alluvial aquifer. The other two single well locations are at a site 1 mile south of Platteville and another site at the CSU-CHILL National Radar Facility, northeast of Greeley. The recovery of the three damaged/dry wells, and the addition of three new sites, now gives the program 23 study sites in the monitoring well network (Fig. 1).

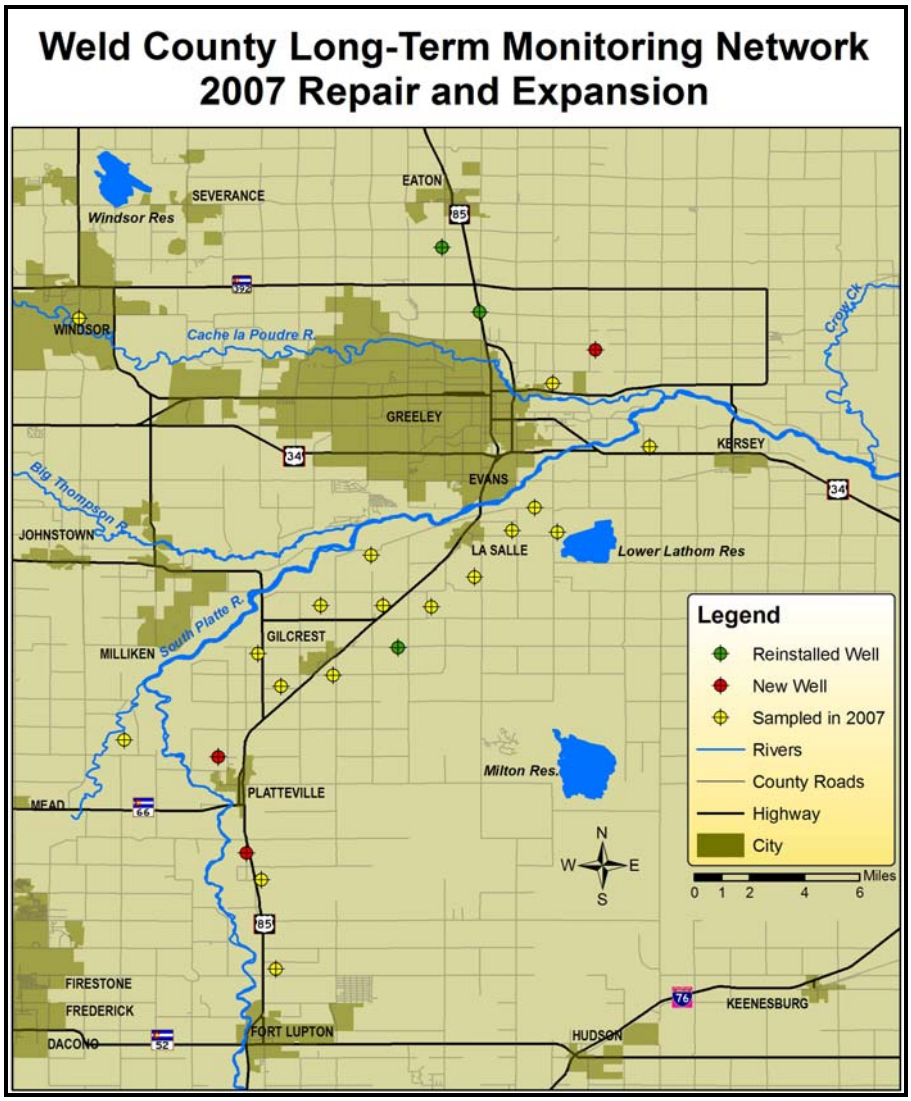

Figure 1. Map depicting locations of repaired (re-installed), new additions, and sampled monitoring wells as part of repair and expansion work in 2007 of the Weld County Long-Term monitoring well network.

2007 Sampling Results

In general, the mean and median nitrate concentration in 2007 is below historical values. As seen in Table 4, the percentage of samples above the EPA drinking water standard of

10.0 ppm is lower in all three networks for samples collected in 2007. Only one irrigation well sample was below the detection limit for nitrate, which was 0.05 ppm. Historically, only 14 samples have ever had a nitrate result below the detection limit (BDL), and only in the irrigation well network. The maximum nitrate level of 70.70 ppm, in the monitoring well network, is from the same well as the historic maximum of 111.32 ppm. As matter of fact, the lowest concentration for this well since first being sampled, in 1995, was 42.8 ppm back in 1997; however, since the maximum of 111.32 in 2003, the nitrate concentration has decreased every year. As can be seen in Figure 2, all samples collected north of Greeley had nitrate concentrations above 10.0 ppm as well as most of the samples collected between Gilcrest and La Salle.

Weld County Long-Term Project
Nitrate Results by Network

	Irrigation	Monitoring	Domestic
	---------- 2007 ----------		
# Samples	28	17	10
# BDL	1	0	0
% Above MCL	60.7	64.7	30.0
MEAN	14.29	19.33	10.38
MEDIAN	12.30	18.90	7.73
Q1 (25%)	7.35	7.66	4.44
Q3 (75%)	22.45	26.20	17.98
Minimum	4.20	1.68	0.38
Maximum	27.80	70.70	24.70
	---------- 1995-2006 ----------		
# Samples	632	224	66
# BDL	14	0	0
% Above MCL	72.9	70.5	47.0
Mean	17.24	22.96	13.91
Median	16.33	19.15	9.42
Q1 (25%)	9.90	8.21	4.36
Q3 (75%)	24.09	30.49	19.32
Minimum	0.24	1.9	0.25
Maximum	81.98	111.32	51.7

Table 3. Nitrate results for Weld County Long-Term Project by sampled network. **# BDL** is the number of samples below detection limits. **% Above MCL** is the percentage of all samples in which nitrate concentration is above the EPA Drinking Water Standard of 10.0 ppm. All units values are in parts per million (ppm) unless otherwise indicated.

There were a total of seven pesticide detections throughout all networks. The irrigation well network had one well with detections of phosphamidon (0.7191 ppb) and oxydemeton-methyl (1.3498 ppb) and two additional irrigation wells each had dichlorvos detected at a maximum concentration of 0.1408 ppb. One domestic well had a detection

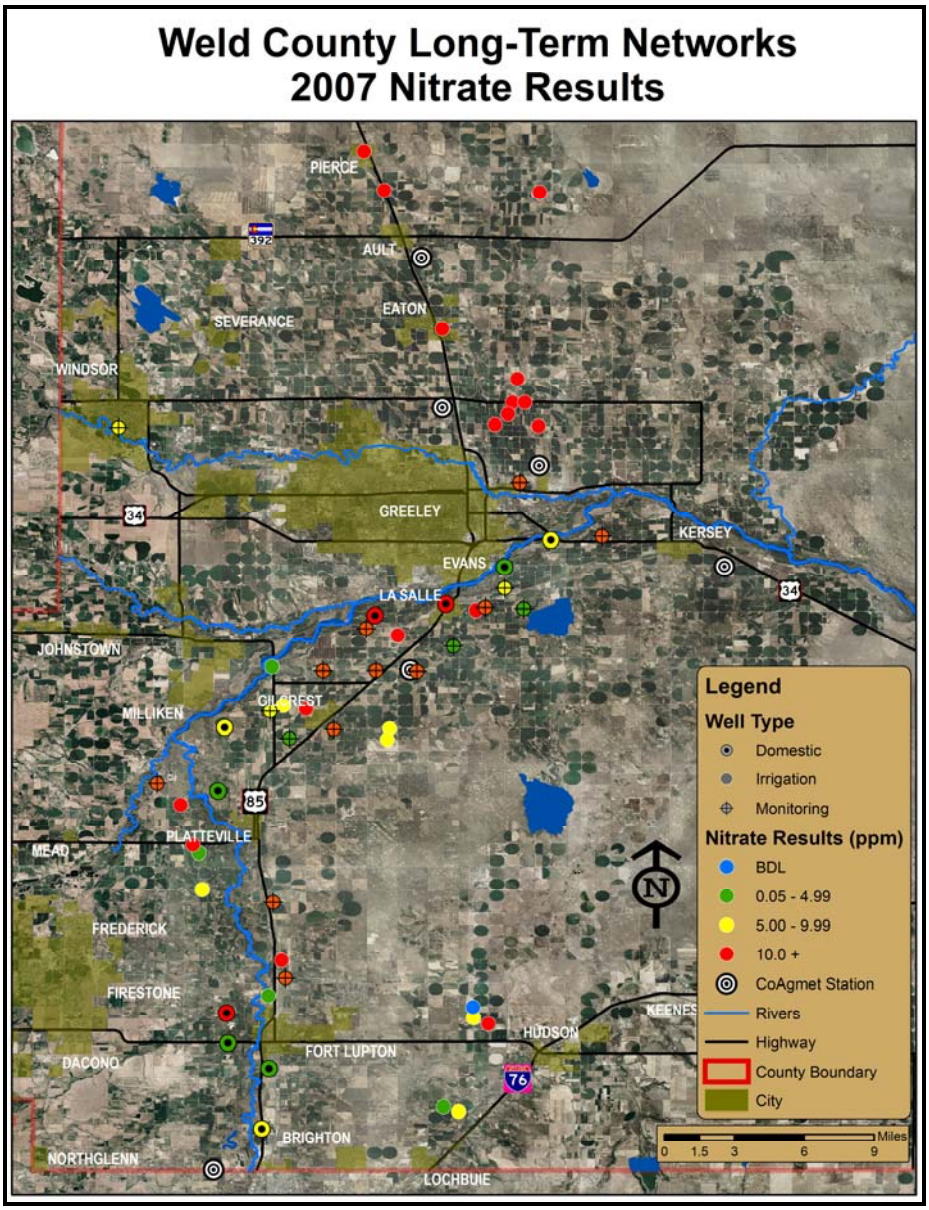

Figure 2. Nitrate results for samples collected from the three well networks constituting the Weld County Long-Term project. CoAgmet Stations collect climatic data for the study area.

of dimethoate at 0.098 ppb and another well had a detection of diazoxon, a breakdown product of diazinon, at 3.138 ppb. Diazinon does have an EPA Health Advisory Level of 0.6 ppb, but exact toxicity information on diazoxon has not been determined. Nevertheless, the domestic well owner will be made aware that diazoxon has been detected in their well.

For the first time since sampling of the monitoring well network began in 1995, there were no detections of atrazine or desethyl atrazine (DEA) (Table 4). As

previously explained, metolachlor, another commonly detected pesticide in Weld County, was not analyzed for in 2007. It is possible that the unexpectedly low number of pesticide detections could be due to the deviation from sampling or laboratory methodology as mentioned earlier; however, preliminary results from trend analysis of long-term data, has shown a downward trend in total number of pesticide detections in Weld County monitoring wells. For 2008, the Program will complete trend analysis on Weld County monitoring well and irrigation well data and will attempt to locate other supporting data (climate data, pesticide/fertilizer use data, and irrigation use data) that might help support the presence of trends. Furthermore, the sampling methodology study previously mentioned will be the main focus for the Program during the sampling of Weld County monitoring wells.

Weld County Long-Term Monitoring Wells
Total Pesticide Detections 1995-2006

Pesticide	'95	'96	'97	'98	'99	'00	'01	'02	'03	'04	'05	'06	'07	All
prometon	7	7	9	5	6	0	0	0	0	0	0	4	0	38
atrazine	9	10	7	6	6	3	8	6	2	3	6	3	0	69
metolachlor	2	4	5	5	6	5	10	6	2	1	3	5	-	54
DEA	-	13	9	9	9	6	5	9	2	6	10	7	0	85
DIA	-	0	0	1	3	1	0	0	0	0	0	0	0	5
bromacil	-	1	0	0	0	0	0	0	0	0	0	1	-	2
DCPA	-	1	0	0	0	0	0	0	0	0	0	0	0	1
metalaxyl	-	0	1	2	1	0	0	0	0	0	0	2	1	7
2,4-D	0	0	0	0	0	0	1	1	0	0	1	0	0	3
hexazinone	0	0	0	0	1	2	2	1	0	0	0	1	0	7
simazine	-	0	0	0	0	0	0	1	0	0	0	0	0	1
clopyralid	-	-	-	-	-	-	0	0	0	1	0	1	0	2
dicamba	0	0	0	0	0	0	3	0	0	0	0	0	0	3
acetochlor	-	0	0	0	0	0	1	0	0	0	0	0	-	1
metribuzin	0	0	0	0	1	0	0	0	0	0	0	0	0	1
Total	18	36	31	28	33	17	30	24	6	11	20	24	1	**279**
# Sample	16	19	19	18	20	19	18	19	19	19	18	17	17	**238**

Table 4. Total detections for 15 pesticides detected in Weld County Long-Term monitoring well samples collected from 1995 to 2007. The monitoring well network consists of 20 monitoring wells sampled annually in early June. Variability in sample size is due in large part to the number of available wells (4 new wells added in 1996); the presence of water in the well; and/or damaged wells. The presence of a (-) signifies that the pesticide was not analyzed for in that year.

Front Range Urban Monitoring Network

The Program completely reassessed the Front Range Urban Monitoring Network (FRUMN), initiated in 2005, and determined that it was necessary to set some criteria for getting more thorough coverage throughout all the major urban areas

across the Front Range. Forty wells were sampled in 2005 and many were clustered in the northern Denver-metro and thus did not provide adequate coverage of the entire Front Range.

After discussion, it was decided that the following cities will be the current focus of the FRUMN: Fort Collins, Greeley, Loveland, Longmont, Boulder, Denver-metro, Castle Rock, Colorado Springs, and Pueblo. The desired number of wells to sample in each city, listed below, was dependent on the population, geographic extent, and achieving a nearly uniform distribution:

- Denver-metro: 45-50 wells
- Colorado Spring: 15-20 wells
- Fort Collins: 10-15 wells
- Boulder, Greeley, Longmont, Loveland, and Pueblo: 5-10 wells each
- Castle Rock: 3-5 wells

Initial cooperation is being sought from public land owners (i.e. local government) in order to minimize the risk of losing property access due to changes in land ownership that more commonly occurs with private land owners. Pre-existing monitoring wells are preferred; however, if the budget permits, installing our own wells is being strongly considered. A well owned by the Program increases the likelihood of long-term well access and monitoring, which is the intent of the FRUMN.

As of January 2008, cooperative agreements have been established with the following entities:

- Fort Collins
    - City of Fort Collins
        - Revocable permit granted for installation of 13 CDA-owned wells
    - Colorado State University
        - Permission to sample one existing monitoring well on campus
        - Permission to install one CDA-owned monitoring well at CSU-ARDEC just south of Wellington
- Greeley/Windsor
    - Central Colorado Water Conservancy District
        - Four existing monitoring wells in Greeley from 2005 effort
        - One existing monitoring well in Windsor
- Denver-metro
    - Denver Water

        - Permission to sample 19 existing Lawn Irrigation Return Flow (LIRF) wells throughout central and western Denver-metro
    - City of Aurora
        - Permission to sample 10+ existing LIRF wells throughout Aurora
    - CO Dept. of Labor & Employment – Division of Oil & Public Safety
        - Permission to sample existing, up-gradient monitoring wells at LUST/TRUST remediation sites managed by the State
    - Metro Wastewater
        - Three existing monitoring wells from 2005 effort
    - USGS
        - Four existing wells in SE Denver-metro
    - Golf Courses
        - Permission to sample two existing monitoring wells on two different golf courses in west Denver-metro
- Castle Rock
    - USGS
        - One existing monitoring well
- Colorado Springs
    - School District 11
        - Established a memorandum of agreement (MOA) and installed 11 CDA-owned monitoring wells on nine school properties in the southern portion of Colorado Springs
        - Two locations have multi-depth wells installed
- Pueblo
    - City of Pueblo – Office of Public Works
        - Permission to sample two existing monitoring wells

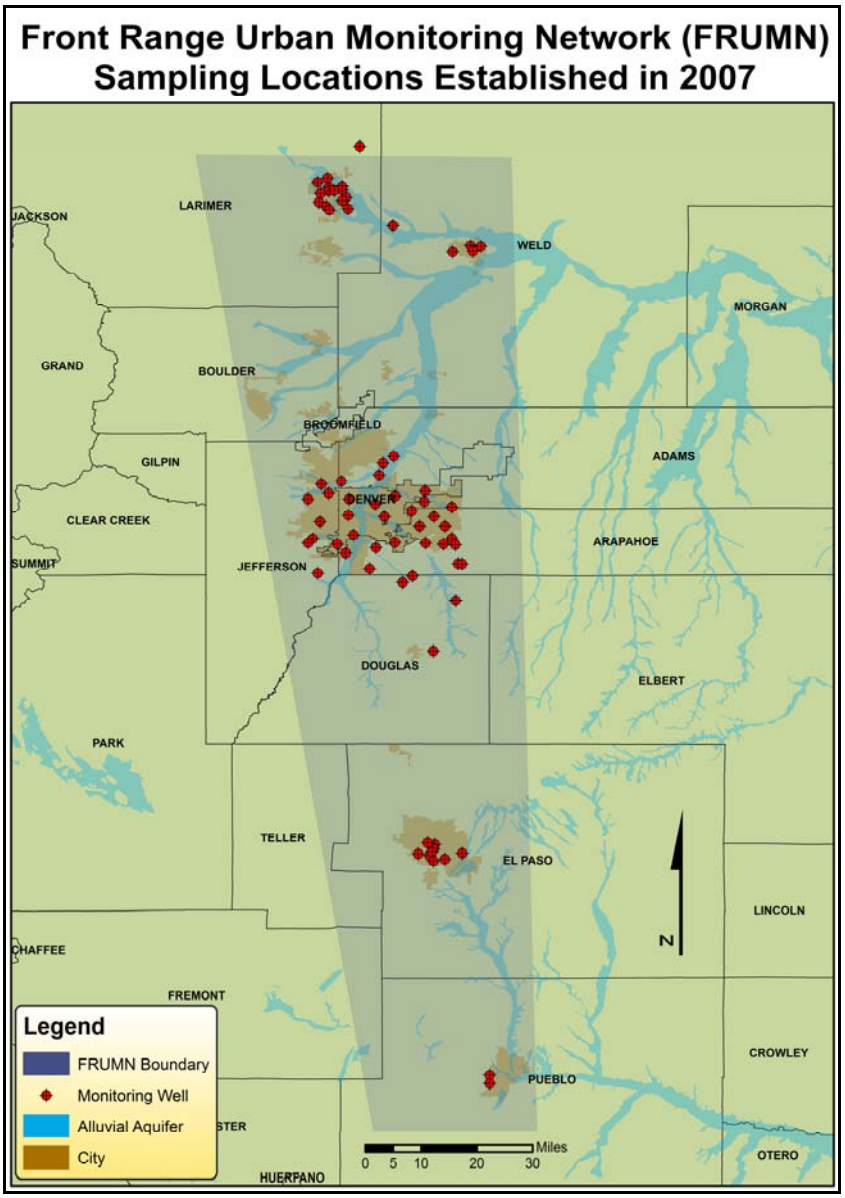

Figure 4. Monitoring well locations established in 2007 through cooperation with various entities in several urban areas along the Front Range.

All monitoring wells in Denver-metro, Greeley, and Windsor were sampled in fall 2007. However, due to complications at CDA's Laboratory, no pesticide results were available for 2007. All of the locations seen in Figure 4 will be sampled in May/June 2008 and analyzed for basic inorganic nutrients, dissolved metals, and 100+ pesticide compounds to establish a proper baseline sampling which will be reported in the 2008 Annual Report.

San Luis Valley

The San Luis Valley (SLV) network consists of 35 monitoring wells that are currently sampled once every seven years through cooperation with the USGS NAWQA Program. The last sampling of this network occurred in 2000 and resulted in 33 wells being sampled and two dry wells. The unconfined aquifer lying in the SLV has suffered from the statewide drought and has dropped in elevation since 2000. Of the 35 wells in the network, 22 had to be re-drilled in the winter of 2007 in order to reach the declining water table which ranged from 7.7 to 22.3 ft deeper. Even then, one of the reinstalled wells was dry by August and could not be sampled in 2007.

Figure 5 shows the locations and difference in total well depth for the re-drilled wells, as well as the locations of the 12 monitoring wells that were not re-drilled. Only 10 of the 12 wells not re-drilled were sampled in 2000 and 2007 and can therefore be evaluated for temporal variability. Data for 21 of the 22 wells reinstalled into new, deeper locations in the aquifer, and sampled in 2007, will be interpreted as new baseline data since it can not be confirmed that drilling the well deeper is what affected the change in nitrate concentration at a particular location, especially since there does not appear to be any correlation between well depth difference and nitrate concentration difference. There does not appear to be a significant decrease in nitrate concentration from 2000 to 2007 in the 10 wells not reinstalled, although the median did drop by nearly 78% (table 6). On the other hand, statistics for the 21 re-drilled wells or the SLV as a whole (Wells-All), may suggest that nitrate concentrations have declined in the last six years, especially since the maximum concentration was decreased by half in 2007. It is important to remember though, that a majority of the wells sampled in 2007 had been reinstalled deeper in the aquifer. The maximum nitrate concentration, in both 2000 and 2007, came from the same well – a well that was drilled more than 11 ft deeper in 2007.

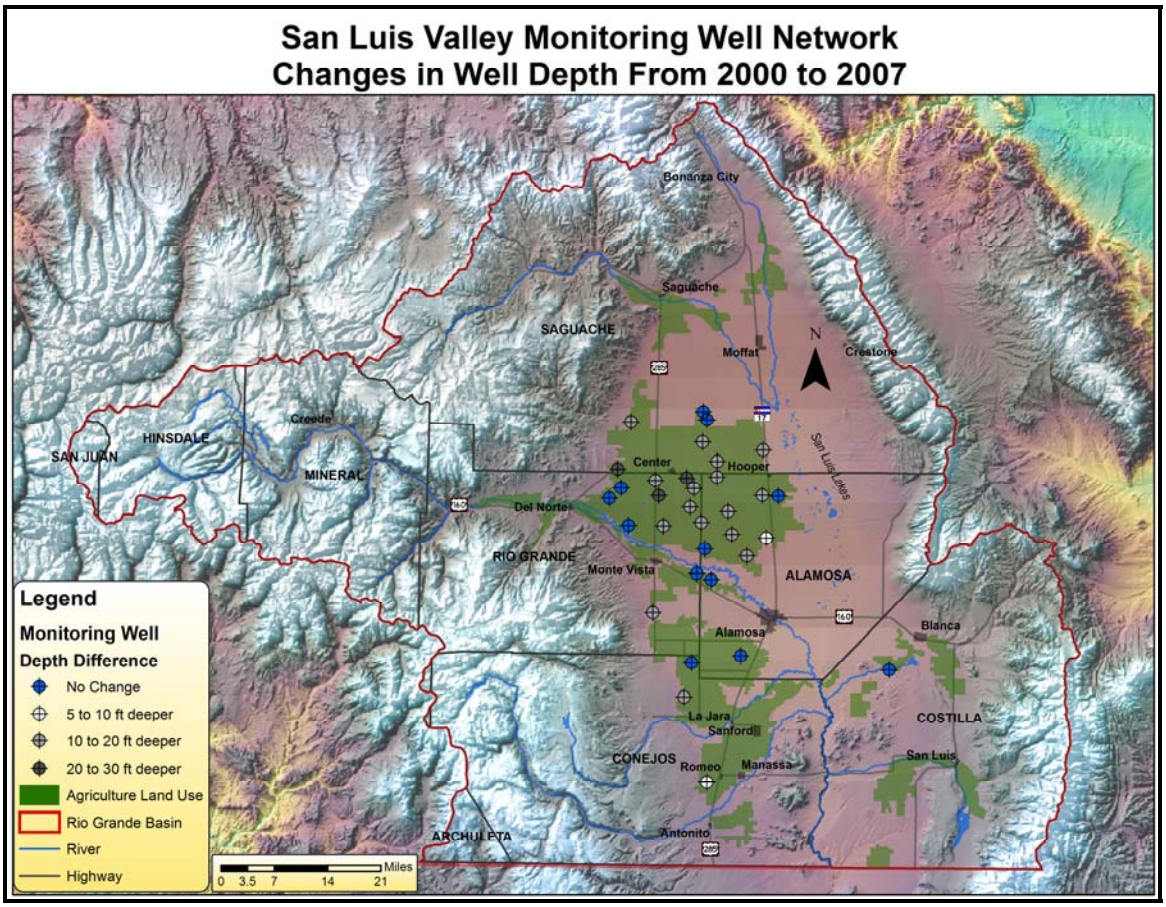

Figure 5. Monitoring wells in the San Luis Valley we're reinstalled in 2007, since their last sampling in 2000, due to a declining water table surface. Wells were reinstalled in the same location but deeper to again access the surface of the unconfined aquifer.

Detectable Nitrate Concentrations in SLV Monitoring Wells						
	10 Wells - Same Depth		**21 Wells - Deeper in 2007**		**Wells – All**	
	2000	2007	2000	2007	2000	2007
Mean	6.49	6.69	10.11	7.96	9.33	7.61
Median	3.39	0.75	3.90	5.65	3.90	1.23
Q1 (25%)	0.32	0.28	0.36	0.38	0.35	0.33
Q3 (75%)	8.74	7.05	14.48	12.20	15.20	12.20
Minimum	0.15	0.13	0.07	0.09	0.07	0.09
Maximum	22.20	25.70	61.01	32.90	61.01	32.90

Table 6. Nitrate data for monitoring wells sampled in the San Luis Valley (SLV) in 2000 and 2007. Twenty-one sampled wells in 2007 were re-installed to deeper depths in the unconfined aquifer, while depths of 10 other wells were unchanged from 2000 to 2007. Statistics only include detectable quantities of nitrate. All values are parts per million (ppm).

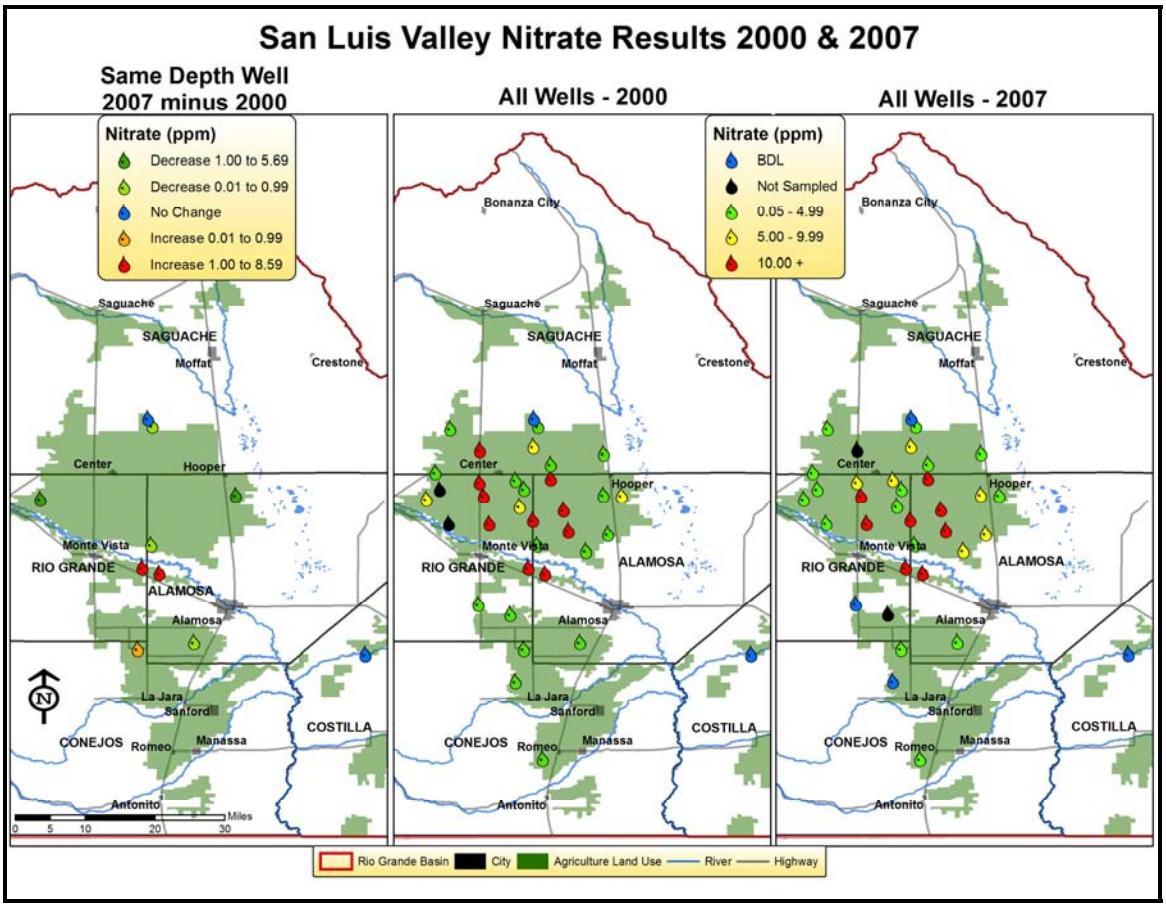

Figure 6. Maps of nitrate concentrations for monitoring wells sampled in the San Luis Valley in 2000 and 2007. Ten wells were sampled at the same depth in both years, while 21 other wells were reinstalled deeper into the aquifer for 2007.

Mapped data from 2000 and 2007 does not show much difference in the number of wells with nitrate greater than the EPA Drinking Water Standard of 10.0 ppm from one sampling event to the next, especially in the center of the SLV (figure 6). Knowing the location of groundwater with nitrate above the standard is important in areas where human consumption may occur. Pregnant women and very young children are especially susceptible to health problems caused by drinking water containing elevated nitrate.

SLV Pesticide Detections - 2007			
Well ID	**Pesticide(s) Detected**	**Well ID**	**Pesticide(s) Detected**
MW-1	Simazine	MW-21	metalaxyl, metolachlor
MW-8	Metribuzin	MW-22	metalaxyl, metolachlor, metribuzin
MW-9	Metribuzin	MW-23	metolachlor, metribuzin
MW-11	Metribuzin	MW-24	metolachlor
MW-14	metolachlor, metribuzin	MW-25	metolachlor
MW-15	metolachlor, metribuzin	MW-27	metolachlor
MW-16	Metribuzin	MW-34	ethoprop, simazine
MW-17	metolachlor		

Table 7. Pesticides detected in monitoring wells sampled in the San Luis Valley (SLV) in 2007. Detections are based on USGS' interpretation of the results.

The number of pesticides detected and the number of wells with pesticides was determined from USGS' methodology which differs from CDA's, as it may include estimated values which are generally below the minimum detection limit. CDA only reports pesticide concentrations that can be quantified which can only happen when a detected quantity is above the minimum detection limit. Therefore, the number of pesticide detections by USGS may differ from the number declared by CDA. Table 7 shows the pesticides detected according to USGS' interpretation. There was a total of 22 pesticide detections in 15 of the 33 sampled wells. Five wells had two pesticides detected while one well had three pesticides detected. The remaining nine wells had only one detected pesticide. In 2000, there were 14 total pesticide detections with nine being of metolachlor and five being of metribuzin.

CDA Biochemistry Standards Laboratory
2007 Minimum Detection Limits

Common Name	MDL	Common Name	MDL	Common Name	MDL
2,4-D	0.090	dimethoate	0.058	parathion-OA	0.067
2,4-DB	0.151	disulfoton	0.010	pebulate	0.056
3-OH carbofuran	0.045	endosulfan alpha	0.111	pendimethalin	0.056
Acifluorfen	0.080	endosulfan beta	0.111	phorate	0.006
Aldicarb	1.500	endrin	0.049	phorate sulfone	0.033
aldicarb Sulfone	0.200	EPTC	0.027	phorate sulfoxide	0.333
aldicarb Sulfoxide	0.005	esfenvalerate	0.556	phorate-OA	0.011
Aldrin	0.056	ethalfluralin	0.222	phosphamidon	0.200
Atrazine	0.111	ethoprop	0.005	picloram	0.447
Benfluralin	0.111	fenamiphos	0.030	p-p'-DDE	0.006
bensulfuron methyl	0.054	fenamiphos sulfone	0.216	prallethrin	0.056
Bentazon	0.209	flumetsulam	0.128	profenophos	0.067
Bifenthrin	0.011	heptachlor epoxide	0.111	prometon	0.556
Bromoxynil	0.038	hexazinone	0.167	prometyrne	0.167
Butylate	0.022	imazamethabenz methyl	0.004	propanil	0.556
Carbaryl	0.020	imazaquin	0.009	propargite	0.133
Carbofuran	0.016	imazethapyr	0.007	propiconazole	0.055
chlorimuron ethyl	0.066	imidacloprid	0.042	resmethrin	0.111
Chlorothalonil	0.222	imidan	0.083	simazine	0.333
Chlorpyrifos	0.012	isofenphos	0.050	sulfometuron methyl	0.015
chlorpyrifos methyl	0.015	lambda cyhalothrin	0.167	sulprofos	0.012
chlorpyrifos-OA	0.266	linuron	0.189	tebuconazole	0.060
cis-permethrin	0.036	malathion	0.023	tebuthiuron	0.010
Clopyralid	0.151	MCPA	0.091	tefluthrin	0.011
Cyanazine	0.556	MCPB	0.228	terbufos	0.006
Cyfluthrin	0.833	metalaxyl	0.056	terbufos Sulfone	0.009
Cypermethrin	0.999	methidathion	0.033	tetrachlovinphos	0.050
Cyphenothrin	0.167	methiocarb	0.015	tetradiafon	0.167
DCPA	0.011	methomyl	0.075	tetramethrin	0.167
desethyl atrazine	0.056	metribuzin	0.078	tolclofos methyl	0.007
desisopropyl atrazine	0.222	molinate	0.027	tralomethrin	2.218
Devrinol	0.056	monuron	0.053	triadimefon	0.111
Diazinon	0.007	myclobutanil	0.111	triallate	0.023
diazinon-OA	0.200	neburon	0.075	triclopyr	0.043
Dicamba	0.270	o-p'-DDE	0.018	trifluralin	0.167
Dichlobenil	0.144	oxamyl	0.015	vinclozolin	0.155
Dichlorvos	0.018	oxydemeton-methyl	0.283	nitrate	0.050
Dieldrin	0.056	oxyflurofen	0.167	nitrite	0.050

Table 10. Minimum detection limits (MDL) for 112 pesticide parent compounds and breakdown products analyzed for in 2007 at CDA's Biochemistry Standards Laboratory. All MDL values are in parts per billion (ppb) except for nitrate and nitrite which are in parts per million (ppm).

Laboratory Report

Sampling

There has been considerable work on sampling techniques and preservatives in the past 10 years. The lab will be assisting the program in reviewing, assessing, and updating sampling methods and preservatives. This began in late 2007 and will continue into the 2008 sampling season. We will be comparing preservatives and sampling techniques used to acquire water from the monitoring wells.

Extraction

Similar to the above, there have been advancements in the extraction techniques used to separate pesticides from water. Currently, the lab utilizes the relatively modern approach of solid phase extraction (SPE). In the interest of increasing the program's analyte list and lowering detection limits, the lab proposes to compare a liquid-liquid extraction technique to that of solid phase extraction.

Solid phase extraction has the benefit of being fairly well documented by various groups (Academic, Govt, and Private Labs) interested in pesticide detections in water. It also can provide good selectivity for compounds of interest. It has the weakness of being somewhat limiting with regard to the program's analyte list and also expensive to perform. The SPE cartridges can also provide "spurious" peaks that then have to be ruled out as actual pesticide detections.

Liquid-liquid extraction is an approach that has been employed for a wide range of analytical applications over decades of use. It has the weakness of being more labor intensive, and it must be performed in a fume hood. It has the benefits of extracting both polar and nonpolar pesticides from water (1), it is a simpler approach, it is widely used, and it minimizes the emergence of spurious peaks. Liquid-liquid extractions will be run in tandem with SPEs on select samples and results will be summarized in the 2008 Annual Report.

Analysis

The lab performs analyses using four types of instrumentation, short summaries of each and improvements/recommendations for their application are listed below:

- Ion Chromatography – Nitrate & Nitrite

  The lab utilizes a Dionex Ion Chromatography System. This system is very common in ion analyses and is a good setup for the program.

  Improvements for 2007~

Installed a six-point calibration curve for the reported anions and all nitrate/nitrite detections for 2007 were reported from within the calibration curve (dilutions were performed on high concentration detects for verification and reporting from within the calibrated range of the IC). We also strove to analyze all samples within the 48 hour hold time for nitrate/nitrite.

Recommendations for 2008~
The lab will look to expand the calibrated range of the instrument as there was some indication that we are not utilizing the full capabilities of the Dionex with regard to calibrated concentrations. The range was moved up slightly in 2007 from 0.05 – 10.0 ppm to 0.05 – 28.0 ppm. This will reduce the number of dilutions and enable expedient reporting of the Nitrate/Nitrite results.

- <u>Gas Chromatography Mass Spectrometry – 49 Pesticides</u>
  The lab utilizes an Agilent 5890-5972 gas chromatograph mass spectrometer. A newer instrument, an Agilent 6890-5975 GC/MS is on order and should be delivered to the lab in 2008. This will provide substantial improvements to the lab's GC/MS capabilities.
  Improvements for 2007~
  The lab installed a four-six point calibration table for all compounds and implemented a pesticide-specific searchable library function in the instrument's software for the 2007 sampling season. These are improvements to the identification and quantitation of pesticide detections. This also means accuracy and precision are improved for the program. The number of false positives will decrease.
  Each pesticide of concern has a primary quantitation ion and up to three secondary identification ions. The lab GC/MS identification criteria are:
    1. Pesticide seen at proper Retention Time
    2. Primary Quant Ion is present
    3. At least one of the Secondary Identification ions is present
    4. Ratios of Quant Ion and Secondary ID ion match those of the standards used in the calibration curve.

  The lab also retains a notebook binder of NIST pesticide spectra for reference when working through difficult identifications.

Recommendations for 2008~
The lab would like to expand the number and type of Quality Control Samples for the 2008 season. The program has historically utilized field QC samples to check the lab, which will continue. Lab QC samples (to monitor the extractions and instrumentation) will be added.
Proficiency Testing – The lab is going to begin participating in proficiency testing managed by an independent Standards Manufacturer. The company is called ERA and they manufacture standards for labs and manage/monitor proficiency testing programs nationwide for a wide variety of analytes in a wide variety of matrices. The lab will be involved in the Pesticides in Water PT. One important comment – not every pesticide or analyte of interest will be included in the PT, however we can expect that 60% or greater of the analytes we look for will be in the PT. This has the benefit of demonstrating the lab's proficiency in performing pesticide analyses. It also meets one criterion for ISO17025 accreditation.
New GC/MS for the lab – This new instrument will lower the lab's detection limits. It will also enable us to utilize large volume injections. This is important because the USGS/NWQL has a growing body of work utilizing small sampling filters, methylene chloride extractions, and large volume injections to streamline sampling efforts and improve pesticide detections from groundwater. The lab is working towards collaborating with these efforts at the USGS. The new GCMS will not be fully online until the 2009 sampling season. It will be running in 2008, but due to validation requirements, the lab will not fully implement the unit until the break between the 2008-09 sampling seasons. Look for an update in the 2008 program Annual Report.

- Gas Chromatography Pulsed Flame Photometric Detection – 28 Organophosphate Pesticides

  The lab utilizes an Agilent 6890 Gas Chromatograph with OI Pulsed Flame Photometric Detectors for the analysis of phosphorus-containing pesticides.

  Improvements for 2007~
  The lab expanded the analyte list, previously only four-eight OP pesticides were reported. A four-six point calibration curve was

implemented on the instrument, improving identification, quantitation, accuracy, and precision. Previously two vials had to be provided for this analysis; this has changed to one vial. It is now a single injection split to two columns and two detectors. This was done to decrease the amount of work needed from the extraction technicians and to improve instrumental performance by utilizing the automation capabilities.

Recommendations for 2008~
A review of the analyte list may cause the program to adjust the number of analytes downward to 22 from 28. This is done when there is no evidence of detections in previous year's samples and the compound(s) pose difficulties in extraction or chromatography for the lab.

- Liquid Chromatography Mass Spectrometry (LCMS) – 46 Pesticides
  The lab utilizes a Thermo-Finnigan LTQ LCMS for analysis of a wide range of pesticides not amenable to gas chromatography; most notable are certain herbicides and carbamates. The large list of analytes has many compounds that have never been detected in Colorado groundwater. The LCMS instrument manufacturer, Thermo-Finnigan has notified the lab that the LCMS will now move into a "best effort" support status due to its age.

  Improvements for 2007~
  None, this is a complicated SPE extraction and LCMS analysis that will be reviewed in 2008.
  Recommendations for 2008~
  Review of the current program analyte list to see if it makes sense to cut the list down to 23 compounds. This reduction in workload may enable the lab to add an important analyte, Glyphosate, to the analyte list. Glyphosate requires a unique extraction to analyze it effectively; it is typically performed as its own separate extraction and LCMS analysis. The LCMS analyses will still provide important compounds like 2, 4-D, 2, 4-DB, Clopyralid, Dicamba, commonly used Carbamates, and others.
  The lab requesting proposals from Thermo-Finnigan on the most economical way to replace the current LCMS.

Accreditation

The lab is moving toward accreditation. I am reviewing/updating/writing SOPs for the various procedures in the lab. Many of the improvements listed above are geared toward gaining accreditation for the lab. This is both a significant effort and long-term process. The cycle of application for accreditation begins in 2008, while the lab may not be fully accredited within one single year, we will be well on the way.

References

(1) EPA Method 507 – Determination of Nitrogen and Phosphorus-containing Pesticides in Water by
Gas Chromatography with a Nitrogen-Phosphorus Detector.
EPA Method 508 – Determination of Chlorinated Pesticides in Water by
Gas Chromatography with an Electron Capture Detector.
(Note: both of these methods utilize a liquid-liquid extraction)

2007 Annual Report Colorado State University Extension

Summary of Accomplishments

- Conducted educational programs throughout Colorado on issues related to agricultural chemicals and groundwater quality. Groups addressed include: crop and livestock producers, commercial applicators, chemical dealers, conservation districts, crop consultants, NRCS agency personnel, homeowners, private well owners, real estate professionals, and urban chemical users.

- Worked to coordinate efforts of the Agricultural Chemicals and Groundwater Protection program with other state and federal programs in Colorado.

- Conducted training related to the Colorado Best Management Practices Manual. Distributed publications to Colorado citizens covering nutrient, pesticide, irrigation, manure, corn, pesticide record keeping, and private water well management.

- Conducted a second year of field demonstration and applied research on limited irrigation under three plant populations for grain corn and limited irrigation of wheat following onions.

- Established a new on-farm site near Greeley to demonstrate cover crops as a transition to dryland or permanent grass for land that lost irrigation water.

- Conducted irrigation management demonstrations on farmer fields in the Arkansas Valley. Demonstrations included: using crop water use (ET) from the CoAgMet weather stations network and WaterMark® soil moistures for improved irrigation scheduling.

- Helped CDA establish a new dedicated urban well monitoring network, primarily through communication with cooperating municipalities and other public entities.

- Conducted nitrogen management applied research and demonstrations on farmer fields near Prospect Valley, Colorado for the third year, using the pre-sidedress

soil nitrate test (PSNT) for corn when applied with poultry manure in cooperation with Parker Ag Services Company.

- Continued to cooperate with the Colorado Climate Center to promote and improve the crop water use (ET) reports provided by the Colorado Agricultural Meteorological Network (CoAgMet). See www.CoAgMet.com.

- Served on the Colorado board for the Certified Crop Advisors Program as exam chair responsible for conducting the state exam.

- Maintained a CSU Extension Water Quality Website to disseminate BMP information via the Internet (www.csuwater.info).

- Distributed revised series of four fact sheets on the web to educate Colorado homeowners on BMPs for urban pesticide and fertilizer use.

- Revised, reprinted, and distributed the *Irrigated Field Record Book.*

- Updated the Microsoft Excel® and .pdf versions of the *Pesticide Record books for Private Applicators* and made these products available for download at www.csuwater.info.

- Worked with CDA to finish the development of a web-interactive database utilizing the Integrated Decision Support (IDS) Group at CSU to present the Program's groundwater quality data to the general public and other agencies. See: http://wsprod.colostate.edu/cwis435/WQ/index.html

- Served on the planning committee for the 2007 South Platte Forum. The SP Forum is an interdisciplinary conference that brings together diverse interests in water to communicate and get the latest on water quantity and quality science and policy in the basin.

Ongoing BMP Development and Education

Colorado State University Extension (CSUE) has worked with the Colorado Department of Agriculture (CDA) to develop Best Management Practices (BMPs) for Colorado farmers, landowners, and commercial agricultural chemical applicators. Because of the site-specific nature of groundwater protection, the chemical user must ultimately determine the BMPs adopted for use at the local

level. The local perspective is also needed to evaluate the feasibility and economic impact of these practices. The Groundwater Program Advisory Committee has recommended that a significant level of input be received at the local level prior to adoption of recommended BMPs. Colorado State University Extension has compiled a broad set of BMPs encompassing nutrient, pest, and water management that has been used as a template for local committees. These documents were published in a notebook form in 1995 that are updated as needed (i.e. Private Well Protection was revised in 2005) and expanded to include additional guidelines.

Cooperative Extension piloted the local BMP development process in the San Luis Valley and in the Front Range area of the South Platte Basin. The local working committees consist of a small group of producers, consultants, and chemical applicators. Both of these groups have produced BMPs for nutrient and irrigation management - the most serious problems in their respective areas. In 1995, the Shavano Conservation District worked with local Extension agents and producers to develop a set of practices appropriate for the West Slope entitled "Best Management Practices for the Lower Gunnison Basin". During 1996, a fourth local BMP work group was initiated in the lower South Platte Basin. They published their findings in a bulletin entitled "Best Management Practices for the Lower South Platte River Basin." Although most of these work groups have not been active since finishing their local BMP publications, these guides continue to be distributed at the local and state level. Building on these efforts, a crop specific BMP, "Best Management Practices for Colorado Corn" was published in 2003 with support from the Colorado Corn Growers. Revision of both the Pesticide and Corn BMP's began in 2007.

Field Demonstration and Research

Field demonstration work in 2007 focused on helping growers improve water and nutrient management. One significant project is the second year of a limited irrigation trial in Weld County where we demonstrated limited versus full irrigation on grain corn using three different plant populations (~20, 25, and 32 thousand plants per acre). WaterMark® soil moisture sensors using a Hansen AM400® visual display and logger along with ET from an atmometer were used to schedule irrigations at this site. This work is supported by a USDA/NRCS Conservation Innovation Grant (CIG) that provides additional visibility through this partnership.

Another nutrient management issue involves residual soil N and P in formerly irrigated fields. Reduced irrigation water supply has impacted South Platte River

Basin farm production levels. Irrigation well curtailments have dried up thousands of acres with resultant weed infestation problems - weeds thrive in low water, high nutrient environments. One viable option toward sustainability is to convert formerly irrigated acres to perennial grasslands. This conversion is a process that involves soil nutrient management and weed control to enable perennial grasses to compete in a low soil moisture environment. This marked the second year of demonstrative research conducted at cooperator's farms in Weld County. This research was designed to investigate management strategies utilizing cover crops to transition from an irrigated cropping system to a non-irrigated grassland or dryland cropping system. Cover crops like haymillet, sorghum-sudan, sterile sorghum, winter wheat, and triticale were planted during the 2007 growing season. Weed management and N and P soil nutrient management were made possible with these cover crops. This research will be continued in 2008 and possibly extended into 2009 to better understand and demonstrate the feasibility and advantages of grassland establishment utilizing cover crops. This work was funded in part by the West Greeley Conservation District.

We continue to improve the awareness and usability of crop ET information provided by the CoAgMet weather network. Cooperating with field CSUE faculty and Nolan Doesken in the Colorado Climate Center, we upgraded the usability and output of ET reports from weather stations in the CoAgMet network. Specifically, users now have the ability to choose specific crops, weather stations, and planting dates to customize their reports (see "New ET Reports" link at www.CoAgMet.com). In addition, an additional weather station was added into this network in 2007 near Iliff, Colorado.

The third and final year of a study in cooperation with Parker Ag Services on using the pre-sidedress soil nitrate test (PSNT) for corn in fields amended with poultry manure was conducted in 2007. The PSNT has been used successfully in non-manured fields in Colorado, but had not been extensively tested where manure was applied and no work had been done on fields receiving poultry manure. The trial results suggested that the original PSNT calibrated value is valid on manured fields and would allow farmers to eliminate a sidedress application with confidence when soil nitrate levels are above the critical level of 15 ppm nitrate-nitrogen. An educational dinner was held in February of 2007 to present cooperating landowners information regarding this project.

Education and Communication

Communication to a wide audience is a vital component of the program. Numerous methods are used to provide information to individuals and organizations using agricultural chemicals as well as the general public. We continue to provide written fact sheets and publications with information on the program and distribute at meetings, conferences, and trade shows. Also, a new display booth to use at conferences and trade shows to provide information on the program was purchased and updated in 2007. The updates reflect new projects, water quality data, and staff the program has hired. Information on groundwater protection is continually being presented to the public through publications, newsletter articles, mass media, press releases, and presentations at meetings throughout the state. Presentations on how the program works, past and present water quality projects, and plans for future projects with request for local input are made at every opportunity. In 2007, presentations were made at several major meetings and small local groups throughout the state. Audiences ranged from licensed commercial applicators and Certified Crop Advisors to private well owners and urban homeowners.

This past year, we continued to provide information over the internet. Several locations including the CSU Extension web site (http://www.ext.colostate.edu), and the CSU Extension Water Quality web site (http://www.csuwater.info) provided information on BMPs. In 2007, the Agricultural Chemicals and Groundwater Protection Database Information System was linked to the CSU Extension Water Quality web site: (http://idsnile.engr.colostate.edu/webkit/Groundwater/). This information tool was developed in collaboration with CDA and the Integrated Decision Support Group with the Dept. of Civil Engineering at CSU, with grant funding from EPA. The information tool provides the general public, researchers, and water policy makers with over 15 years of the Program's groundwater monitoring data. This data can be queried in a variety of ways. Outcomes of this project include: improved accessibility and knowledge of water quality data; improved use of resources to protect vulnerable groundwater; a GIS tool for directing future groundwater management efforts at multiple scales; and increased stakeholder awareness and involvement regarding any potential or identified groundwater contamination.

Cooperation with the USDA/CSREES Water Resources program (http://www.usawaterquality.org/) has become a significant activity for the CSU water quality program. This regional program operates with four primary initiatives: Watershed Management, Production Agriculture Water Quality,

Agricultural Water Conservation and Protection, and Drinking Water - Human and Livestock Health. Colorado significantly contributes to the last four mentioned projects. One benefit of this coordination is a significant amount of sharing of expertise, resources and knowledge between the six states. Another benefit is a mini-grant program for Extension field and campus faculty to encourage educational programs and extend research information on topics related to water and water quality. Seven proposals were accepted with the following topics:

- Pesticide drift reduction
- Storm water pollution prevention
- Nitrogen management under drip irrigation in the SLV
- Well testing in under-served audiences
- Private well and drinking water education
- Irrigation audits for homeowners

These mini-grants allow us to reach a wide, more diverse audience in areas of the state that we wouldn't be able to contact otherwise and leverage our normal Groundwater Program with CSREES dollars.

Presentations and Publications

Bauder, T.A. and J.P. Schneekloth. 2007 Revision. Irrigated Field Record Book. Colo. State Univ. CE Bulletin XCM 228.

Bauder, T.A and J.S. Schneekloth – Editors. Limited Irrigation Management – Getting the Most Crop per Drop. From the Ground Up - Agronomy News, Spring 2007 Issue.

Bauder, Troy, Rob Wawrzynski, Dave Patterson, Matt Neibauer, and Reagan Waskom. 2007. Colorado groundwater database. Colorado Watershed Assembly, Sustaining Colorado's Watersheds conference, Breckenridge, CO.

Bauder, Troy, Dave Patterson, Rob Wawrzynski, Greg Naugle and Karl Mauch. 2007. Agricultural Chemicals and Groundwater Protection Program Water Quality Database System (http://ids-nile.engr.colostate.edu/webkit/Groundwater/).

Bauder, T.A., R. Wawrzynski, D. Patterson, M. Neibauer, and R.M. Waskom. 2007. A Web- Based Ground water Quality Information Tool for Colorado. USDA-CSREES, National Water Conference, Savannah. January 31, 2007.

Bauder, T.A., T. Gaines and L. Wu. 2007. Interactions of Linear Polyacrylamide with Hydrophobic Soil – Adsorption and Flocculation Studies. Poster. Am. Soc. Agronomy Abstracts. New Orleans.

Naugle, Greg, Troy Bauder, Karl Mauch, and R. Wawrzynski. 2007. Long-term monitoring strategy and plan for the Agricultural Chemicals and Groundwater Protection Program. Colo. Dept. Ag.

Pritchett, J., N. Hansen, D. Westfall, T. Bauder, J. Ascough III, A. Jha, G. Buchleiter. 2007. Developing Economically Sustainable Cropping Strategies for Small and Medium Sized Farms: An Update. Poster presented at USDA-NRI-Small and Medium Sized Farms Project Directors Meeting, March 8-9, 2007, Washington, D.C.

Quarles, D, T. Bauder, and S.A. Van Wychen. 2007. Managing Poultry Manure Using the Pre-Sidedress Soil Nitrate Test. Water Environment Foundation Joint Residuals and Biosolids Management Conference. Denver.

2007 Annual Report
Colorado Department of Public Health and Environment

The Colorado Department of Public Health and Environment (CDPHE) continues to be actively involved with the Agricultural Chemicals and Groundwater Protection Program. The CDPHE continues to review the Program's monitoring data on an annual basis, and provide input on the results. In 2007, the CDPHE assisted with the subsequent groundwater-sample collection training during the annual Weld County sampling activities. The CDPHE participated in the Program's annual water tour, as well as attended other Program related meetings on an as needed basis.

The CDPHE has also been involved in the Program's development of a Web-based pesticide and groundwater information tool. Activities this past year related to this effort included assisting with final quality control and functionality testing.

Other activities include finalizing the Program's long-range monitoring plan, which outlines the rationale and proposed schedule for the next ten years of groundwater sampling. Factors that were utilized in developing the long-range plan included historical groundwater sampling data, estimates of pesticide and fertilizer use, and the aquifer sensitivity and vulnerability studies developed by the Program. The long-term monitoring plan also contains allowance to address special sampling situations that may arise through cooperative investigations with other agencies, or due to other special circumstances. Assistance with the short-term monitoring plan has included working with Program staff on locating appropriate monitoring locations, based on local hydrogeologic factors, for the Colorado Springs and Urban Front Range monitoring efforts.

The CDPHE also supports the Program by promoting the Program's activities to outside parties. These activities include communicating the objectives of the Program to other State and Federal agencies, interested parties, and Colorado citizens. Reports, educational materials, and other correspondence have been distributed in an effort to develop an awareness of the importance of the Program to the State's efforts in groundwater protection.