**1993 Research Project Abstract**
For the period ending June 30, 1995
This research project was supported by the Minnesota Future Resources Fund.

**TITLE: Optical Brighteners: Indicators of Sewage Contamination of Groundwaters**
**PROGRAM MANAGER:** Ronald C. Spong
**ORGANIZATION:** Dakota County Environmental Management Department
**LEGAL CITATION:** M.L. 93 Chapter 172, Art. 1, Sect. 14, Subd. 11 (i)
**APPROPRIATION AMOUNT:** $157,000

## STATEMENT OF OBJECTIVES

To determine if optical brighteners, as components of domestic wastewaters and consequently potential contaminants of groundwaters, can be detected in private drinking water supplies and, therefore, utilized as specific indicators of sewage pollution and correlated with more ubiquitous contaminants (e.g., nitrates and coliform bacteria). Also, to ascertain if optical brighteners interfere with atrazine herbicide detection methods resulting in false positives if atrazine is actually below detection limits.

## RESULTS

A fluorometric detection system for optical brighteners (fabric whitening agents) has been designed and tested in a variety of small communities and a number of soil, bedrock and groundwater environments throughout southeastern Minnesota. Immersion filter holders containing cotton and other adsorbent media were placed in the reservoirs of the most used toilets in residences, as well as in other suitable locations, and collected after different exposure periods. In-line filters and syringe filters were also utilized to evaluate shorter filter media exposure times. Exposed cotton and other filter media were analyzed in solid phase with a scanning spectrofluorophotometer with optimum emission wavelength of 440 nm. The resulting excitation, emission and synchronous spectra were computer processed, imaged and peak-fitted to yield data which could be more objectively evaluated along with pertinent observations of each site and the results of drinking water supply testing. In all, twenty small communities and 109 individual sites were evaluated to confirm that selective filter media adsorption and solid phase fluorometry can detect very low levels of optical brighteners (approximately 3 to 5 micrograms per liter as optical brightener equivalents). The optical brightener screening method (immersion filter holders) may be a useful adjunct to conventional sanitary drinking water supply testing parameters, but it is limited to qualitative assessment, i.e., present or not present. However, the in-line and syringe filter media methods hold promise for potential semi-quantitative results in optical brightener equivalents as volume is measured, but they require additional investigation. Likewise, there are no conclusions yet from investigations into whether certain optical brighteners with triazine structures interfere with atrazine herbicide detection methods causing false positive results if atrazine is below method detection limits.

## PROJECT RESULTS USE AND DISSEMINATION

Preliminary results of this investigation were presented on November 8, 1994, at the annual conference of the American Water Resources Association in Chicago, Illinois. Two papers (methodology and field data) were presented on June 7, 1995, at the 26th Congress of the International Association of Hydrogeologists in Edmonton, Alberta, Canada, and were published in the Proceedings. The final report will be formatted into methodologic and case-history papers for presentation at professional conferences and/or publication in peer-reviewed journals. In addition, individual summaries of each community's investigations will be prepared and mailed to participants and state, regional and county environmental health agencies. Aspects of the results of this investigation are already being utilized in MPCA and State and federally funded County studies of individual sewage treatment system impacts on subsurface waters.

Date of Report: July 1, 1995 (Revised)

LCMR Final Report - Detailed for Peer Review - Research

I. Project Title: W oth-2 OPTICAL BRIGHTENERS: INDICATORS OF SEWAGE CONTAMINATION OF GROUNDWATERS

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A. Legal Citation: M.L. 93 Chpt. 172, Art. 1, Sect. 14, Subd. 11 (i)

Total Biennial LCMR Budget: $157,000

Estimated Balance: $23,000*
*Liquidated amount-to-date: $90,671.67 (disbursed to Dakota County as of June 1995). Additionally, estimated amount encumbered-to-date: $43,328.33

Appropriation Language as drafted 7/27/92: This appropriation is from the future resources fund to the commissioner of the pollution control agency for a contract with Dakota County to study the correlation of optical brighteners present in domestic sewage from detergent use with non-agricultural nitrogen as interferences with atrazine detection.

B. LMIC Compatible Data Language: During the biennium ending June 30, 1995, the data collected by the projects funded under this section that have common value for natural resource planning and management must conform to information architecture as defined in guidelines and standards adopted by the information policy office. Data review committees may be established to develop or comment on plans for data integration and distribution and shall submit semiannual status reports to the legislative commission on Minnesota resources on their findings. In addition, the data must be provided to and integrated with the Minnesota land management information center's geographic data bases with the integration costs borne by the activity receiving funding under this section.

C. Status of Match Requirement: Not applicable.

II. Project Summary

The overall objective is to determine if optical brighteners, organic blue dyes added to detergents to enhance the apparent cleanliness of clothing and, consequently, a component of domestic sewage, can be correlated with other wastewater contaminants, such as nitrates, in groundwaters.



Tests of drinking water supplies derived from several karst groundwater aquifers in southeastern Minnesota have detected low levels of optical brightener fluorescence, as well as indicators and contaminants of domestic sewage origin. By extending the testing to wells in other shallow and intermediate depth aquifers throughout a nine-county area, it is hypothesized that optical brightener levels may cost-effectively predict the on-site sewage system contribution to the deterioration of drinking water quality as compared with agricultural sources with the same contaminants but no such dye use.

An inexpensive detector placed in toilet tank reservoirs to adsorb optical brighteners present in water supplies will be evaluated to determine if it can reliably screen for the qualitative presence of domestic sewage contaminants. Also, possible triazine herbicide residue test interference by optical brighteners may account for some false positive tests in areas of pesticide contamination and other areas with no reported triazine use and will be investigated.

III. Statement of Objectives

A. Conduct optical brightener monitoring program.

B. Evaluate monitoring data and information.

IV. Research Objectives

A. Title of Objective: Conduct optical brightener monitoring program.

A.1. Activity: Conduct field investigations, testing and sampling.

A.1.a. Context within the project: The comprehensive monitoring program for optical brighteners relies upon extensive field work to acquire sufficient data and information from a representative sample of individual well water supplies throughout southeastern Minnesota. A number of different unconsolidated and consolidated formation aquifers of shallow to intermediate depth will be monitored to determine their susceptibility to contamination by optical brighteners, domestic sewage indicators and parameters from other pollution sources including agricultural pesticides.

A.1.b. Methods: The study areas will be selected in nine southeastern Minnesota counties (Dakota, Dodge, Fillmore, Goodhue, Houston, Mower, Olmsted, Wabasha and Winona) to represent a number of shallow and intermediate depth groundwater aquifers with different unsaturated and saturated zone thicknesses and compositions. The study areas will include a range of population densities, land uses and perceived or known problems, as well as different types of well construction and drinking water supply systems.

Environmental specialists and technicians will be trained to conduct sanitary surveys of selected individual well water supplies, sewage systems and building occupancies which include:
1. Well construction, protection, abandonment, sealing;
2. Water supply system components (plumbing, storage, treatment);
3. Cross-connection control, backflow/backsiphonage protection;

4. Pollution sources (sewage system, dry well, fuel tank, etc.);
5. Water consumption, use, previous test results, problems;
6. Detergent use and disposal (other optical brightener sources);
7. Consumer health/acceptance, anecdotal information on illness;
8. Field testing and measurements; and
9. Representative sampling for laboratory analysis.

A questionnaire will be developed addressing pertinent elements of the above survey items and will be administered to study participants by trained personnel. In particular, the questionnaire will request information on both current and historical water usage, waste disposal, detergent selection, laundry regimen and other events, behaviors and choices that may be related either directly or indirectly. Anecdotal information will also be recorded to verify observations and permit working hypothesis modifications.

In most cases, the sanitary surveys of individual water supplies will be completed during sampling and field testing to ensure the control of those attributes which may otherwise bias or confound the study results or their interpretation. These include dual water supplies, cross connections, backflow and backsiphonage, recent or continuous disinfection, water treatment devices and unused, abandoned wells. A coded survey form will be developed to facilitate checking for State code compliance (e.g., Minnesota Agency Rules, Chapters 4715, 4725 and 7080), as well as appropriate, known municipal ordinances, and expedite computer data entry.

Particular attention will be focused on the components of the wastewater system to determine if two or more systems exist. For example, an upper story drainfield treatment area and a separate basement dry well disposal would indicate that laundry wastewater may be more directly entering the domestic water supply because of the proximity of the well to the disposal source. Also, other types of waste disposal will be investigated (dumps, etc.) where optical brighteners could possibly be released in addition to building sewage.

Field testing will be accomplished at each site to ensure the representative sampling of groundwater for laboratory analysis. This will include stabilization tests for temperature, specific conductance, pH and oxidation-reduction potential utilizing a YSI 3560 Water Quality Monitor. Field, as well as laboratory, testing may be conducted for certain parameters utilizing a Hach DR/EL-2 Environmental Laboratory (modified with borosilicate glassware, etc.) if subject to change due to destabilizing conditions (e.g., low or high pH, reducing or oxidizing environment and high carbon dioxide and/or low or high oxygen partial pressures).

Field fluorometric analyses may be performed at certain sites to determine background fluorescence, identify possible interferences and verify problems and assumptions. Also, first-draw (collection after 8 to 12 hours of no water use to represent worst-case scenario) sampling may be conducted for metals (e.g., lead and copper) where the sanitary survey or stabilization test results suggest the possible corrosion of plumbing, fixtures and appliances.

Grab samples will be collected, preserved, stored and handled in accordance with approved U.S. EPA (Environmental Protection Agency) METHODS and STANDARD



METHODS whether analyzed by study or contract laboratory personnel. Chain-of-custody procedures will be followed to ensure sample data integrity and compliance with the study's quality assurance plan. Duplicate samples will be collected at random to facilitate replicate and standard addition analyses. Also, trip and field blanks will be utilize for certain analytes which are subject to field or laboratory contamination, volatilization or other problems.

Sites selected for resampling may have the reservoirs of high-use toilets cleaned and chlorinated to allow for the installation of unbleached, undyed cotton detectors for long-term monitoring of optical brighteners. Qualitative adsorption of dye by the detector over time will be compared with the quantitative results, as well as other parameters of contamination. Verification of this qualitative screening method may also be tested by installing detectors at sites both before and after groundwater sampling and field analysis. Experimentation with different screening methods will be conducted concomitantly to assess selectivity, sensitivity, cost and other factors.

Also, sites will be carefully evaluated with respect to soil and bedrock geology and hydrology, topographic characteristics, surface water drainage and wetlands, land-use history and other information pertinent to the study. Possible movement of wastewater in the unsaturated zone will be reviewed to determine the likelihood of migration to groundwater discharge points different than the source location. Verification may be made in some cases by utilizing other tracers or increasing the number of sites sampled to include adjacent and downgradient water supplies.

A.1.c. Materials: Field materials necessary to accomplish this objective include vehicles, topographic maps, soil surveys, surveying instruments, soil coring tools, water sampling stabilization instruments, portable environmental laboratories, sample containers and coolers, portable fluorometers and equipment, unbleached cotton detectors, chlorine bleach, distilled water, field notebooks, calculators and survey, test and sampling forms.

A.1.d. Budget: $57,000
Estimated Balance: $ 0

A.1.e. Timeline: 7/93 1/94 6/94 1/95 6/95
Design program **********
Conduct field work ************************************************

A.2. Activity: Conduct laboratory analysis and quality assurance.

A.2.a. Context within the project: The laboratory analysis of samples of individual water supplies collected during the field investigations will form the majority of the data on optical brighteners, pollution indicators, contaminants and background parameters required for the evaluation phase of the study.

A.2.b. Methods: Analyses will be divided between a project fluorometry and physicochemistry laboratory and one or more more contract environmental laboratories. Laboratories utilized for the analysis of Safe Drinking Water Act parameters will be currently registered or otherwise approved by the Minnesota Department of Health Division of Public Health Laboratories.

Approved analytical methods will be utilized for all required bacteriological and physicochemical parameters in accordance with the current editions of STANDARD METHODS, EPA METHODS or other accepted consensus standards. Additionally, laboratories will have a quality assurance/quality control program which will be reviewed periodically to ensure that data generated by the study meets accepted standards and practices.

The fluorometry laboratory will be established to expeditiously handle photosensitive samples and optimize fluorometric techniques in the analysis of optical brighteners. Controls will include reference samples of optical brightener dyes and detergent formulations containing such dyes. Utilizing narrow pass and sharp cut filters, mercury vapor lamps emitting at 365nm, matched cuvettes and temperature-controlled sample holders, fluorometer specificity and sensitivity will be enhanced allowing accurate and precise analyses. Other filters and lamps will be utilized to evaluate other fluorescent chemical species that may interfere with optical brightener detection. A scanning spectrofluorometer will be sought to facilitate such work, as well as to possibly aid in the separation and identification of similar fluorescent blue dyes.

The bacteriological and physicochemical parameters to be analyzed for a majority of the samples collected include: laboratory pH, laboratory temperature, laboratory specific conductance, total dissolved solids, total and calcium hardness, total and bicarbonate alkalinity, chloride, sulfate, nitrate, nitrite, ammonia, Kjeldahl nitrogen, orthophosphate, total phosphate, silica, sodium, potassium, iron, manganese, total and fecal coliform bacteria, fecal streptococcal bacteria and heterotrophic bacteria (standard plate count). In addition, some selected samples will be analyzed for metals (e.g., lead, copper and chromium), triazine herbicides and volatile organic compounds related to study objectives.

Minnesota Department of Health and Minnesota Department of Agriculture-approved methods for the analysis of triazine herbicide residues will be evaluated with respect to the determination of possible false positives. Reference samples of commercial triazine products will be utilized where appropriate and obtainable, as well as optical brighteners, to test the hypothesis that under some conditions optical brighteners may mask, interfere with or be mistaken for atrazine or other triazine herbicides. In addition, other similar compounds (e.g., cyanuric acid and melamine) that may be used and disposed of in sewage systems will be evaluated. Organic chemists (Minnesota Department of Health, Minnesota Department of Agriculture, University of Minnesota and others) specializing in herbicide residue analyses will be consulted to approve the study design, protocols and data interpretation.

Unbleached cotton detectors will be evaluated qualitatively by developing desorption techniques and fluorometrically scanning for excitation and emission wavelengths. Although it is not likely to be directly quantitative, a variety of techniques may be evaluated to determine if the results can be quantifiable should the volumetric flow be known.

A.2.c. Materials: Laboratory materials required to meet this objective include a fluorometer and appurtenant equipment and supplies, wet chemistry instruments and supplies, refrigerator/freezer, reference samples, reagents, distilled water and data [illegible]s. Specific contracts with approved environmental laboratories will be required.



A.2.d. Budget: $75,000
Estimated Balance: $17,000

| A.2.e. Timeline: | 7/93 | 1/94 | 6/94 | 1/95 | 6/95 |
|---|---|---|---|---|---|
| Set up fluorometry lab | *************** | | | | |
| Contract labs selected | *********** | | | | |
| Conduct sample analyses | | ************************************************* | | | |
| Review quality assurance | | *** | *** | *** | *** |

A.3. Status:

A.3.a. Problems:

The Dakota County Board of Commissioners approved a contract on July 27, 1993, for project cost reimbursement with the Minnesota Pollution Control Agency, and all signatories to the document completed their approvals by September 30, 1993. However, the project did not begin immediately because of a number of problems.

Delays in full project start-up were administrative, contractural and logistical and persisted until March, 1994, when the program manager was assigned nearly full-time for the remaining 16 months. A reallocation of his supervisory duties to a senior staff member was necessary to continue ongoing environmental management program development and operations. Other internal reassignments were completed which included the elimination of the full-time temporary position that had been budgeted to provide the project's technical field support. In retrospect, such field support would have allowed more efficient use of the program manager's time.

With the exception of contract and purchased services, all program activities were accomplished by the program manager. Because of resource problems continuing through January, 1994, departmental administrative approval was given to assign the program manager 80 percent of full-time to the project (3341 hours) with Dakota County contributing 25 percent (835 hours) and the State funding 75 percent (2506 hours). However, by the end of the biennium, the program manager had worked 4143 hours on the project with 2740 hours supported by State funds and 1403 hours unpaid.

Administratively, it has been recommended that Dakota County support the program manager on a part-time basis during the remainder of 1995 to complete the data analysis and database management aspects of the project and to facilitate the presentation and publication of the final reports and research papers.

In the fall of 1993, the program manager completed setting up a Turner 111 fluorometer for field and laboratory analysis of aqueous samples (direct and elutriated) optical brighteners, as well as other dyes. As preliminary development of the detection system ensued, it became apparent that ambient groundwater concentrations of optical brighteners in the areas evaluated were very low, probably due in part to several years of above normal precipitation. Also, it appeared that naturally occurring (e.g., humic and fulvic acids) and other synthetic dissolved organic carbon compounds having fluorescent properties in the wavelength range of 200 to 450 nanometers (nm) interfered with low level optical brightener detection.

In consultation with Professor E. Calvin Alexander of the University of Minnesota Geology and Geophysics Department, the utilization of the Hydrogeochemistry Laboratory's recently acquired Shimadzu RF5000U scanning spectrofluorophoto-meter was requested. Capable of computer-processed, simultaneous excitation, emission and synchronous scans of both aqueous and solid phase samples, the instrument could possibly resolve the problem of low optical brightener detection limits and interfering fluorescent dissolved organic carbon compounds (FDOC's). A contract with the University of Minnesota was approved on February 2, 1994, by the Dakota County Board of Commissioners. The contract amount of $32,519 included scanning spectrofluorophotometry and the services of a graduate student, Steffan Fay, and a Junior Scientist, Scott Alexander. The contract resolved the problem of purchasing (cost: $30,000) and setting up a scanning spectrofluorophotometry laboratory for the project. Professor Alexander was consulted throughout the project period even though he was on sabbatical to New Zealand during the academic year 1994-1995.

The key to the project's success was the public's acceptance and participation. Overall, an average of 20 percent of the building occupants contacted by the program manager agreed to allow access to their premises to install and retrieve filter holders, sample water supplies and inspect utility (wells and water supply lines, waste and wastewater disposal and treatment, etc.) construction and operation. The acquisition and maintenance of sampling sites significantly impacted and limited project time and resources for a number of reasons.

There were many problems with public, door-to-door queries in rural areas, including the following examples:

1. The program manager's Dakota County picture identification card created some confusion and perhaps resistance south of the Cannon River, and a generic LCMR or Minnesota identification card may have met with greater acceptance;
2. A brochure was prepared, distributed and modified but was ineffective compared with a door-to-door, personal touch in securing potential participants. The latter approach, while more time consuming as it meant prolonged contact or repeated visits to speak with spouses, etc., was decidedly more successful;
3. The offer of free water supply testing was often greeted with scepticism and even suspicion. Potential participants would only consider such testing if the results were confidential with limited access by others, especially local and state health and environmental agencies. In fact, it was the program manager's affiliation with the latter agencies that terminated many queries because of public paranoia concerning the condemnation of contaminated wells, failed sewage systems and other waste disposal devices which were the subjects of investigation;
4. Often both spouses or both renters and owners needed to hear the details and approve of them otherwise the return site visit would be unwelcomed and/or would find the filter holder discarded. In particular, permission from the male half of an occupancy proved to be critical confirming that rural life is still male-dominated;
5. Lifestyles, including both spouses working and other out-of-home activities, made it difficult to schedule access for sampling and required the program manager to work weekday early mornings and evenings, weekends and holidays. Frequent, missed appointments were particularly time consuming and resource wasting because of the large project area;
6. Complete access to buildings and property was denied in many cases with the owners' veracity offered in place of the program manager's inspections. This invariably led to unverifiable assumptions that the program manager was hoping to avoid by comprehensive sanitary surveys; and
7. Over the course of the project, property transactions, divorces, deaths and major illnesses significantly altered site accessibility and relationships with participants.



The task of inspecting and sampling 200 sites scattered throughout the nine-county southeastern Minnesota area was demanding as originally planned but should have been revised when the technical support position was eliminated, project startup was delayed and problems with sampling media and fluorometric analysis were determined. Consequently, during the late spring and summer of 1994, the program manager curtailed most new site acquisition and focused on nearby sites to reduce time, mileage and expenses and to focus on accessible, established sites. By the late fall of 1994 and winter of 1995 when most of the problems were resolved and new discoveries were made, there was insufficient time to reasonably acquire a total of 200 sites. A conscious decision was made to elaborate on the 20 communities already being studied by enrolling additional sites and by resampling to enlarge the database for more detailed analysis. Subsequently, only 109 of the planned 200 sites were enrolled. The decision was also made to exclude the approximately 30 randomly selected sites when continuing problems with participant enrollment emerged, as well as cultural changes not reflected on outdated topographic maps (10 to 30 years old) and other information utilized for randomization.

Although the project became more limited in scope with respect to number of sites and communities, the program manager attempted to offset that impact by ensuring the variety of variables represented and thus rigorously test the working hypotheses. Early project work focused on prospecting the southeastern Minnesota area for uniquely different communities in a variety of topographic, hydrogeologic and other environmentally variable settings, and eventually 37 potential candidate areas were found from which 20 communities were selected. The remaining communities and potential participants are available for continued study should funds be made available. Staff limitations also precluded an independent, internal evaluation of the project, and the program manager relied upon the reviews of and discussions with colleagues.

To improve acceptance by potential participants, it was necessary to modify and simplify the questionnaire and the sanitary survey. Instead of working from and filling out forms, questions were verbalized to personalize the interaction with potential participants and improve the chances of enrolling sites. The informal and personal approach proved to be successful for soliciting participation. Replies to leading questions prompted more specific questions. The program manager carefully explained pertinent facts and recommendations to address concerns inevitably raised by participants. The resulting dialogue with over 500 potential participants was revealing and not very flattering of government officials.

Obviously, the public's need to know and understand environmental health and safety facts and issues is very significant but is largely unmet by public resources. An environmental folklore has developed in its place which trivializes or distorts facts, perpetuates unreasonable fears, dismisses genuine concerns and both confuses and frustrates the public. Doubtful or bogus remedies and harmful habits or practices continue, aided and abetted by questionable commercial products, inaccurate advertising claims, poorly skilled service technicians and salespersons, disreputable contractors and do-it-yourself installations and repairs. Consequently, problems related to water supply and waste disposal systems are increasing.

Government has been largely ineffective in dealing with such problems because it is process rather than performance driven, is slow to adapt to new science and technological change and is reticent in its communication with and education of the public it serves. The public's perception of governmental agencies and officials is one of problem "makers" not of problem "solvers". Many persons interviewed by the program manager expressed a serious distrust of government because of past experience or rumors. Although bad experiences can be less easily discounted, rumors propagate because of fear or misunderstanding and are often given credence, in the absence of fact, by those with vested interests. To make a discernable impact, government needs to emphasize the humane, personal approach where honest interactions earn trust and mutual respect, as well as solving problems, rather than the impersonal, self-serving approach that can defeat even the best intentions.

Often, potential participants did not allow complete access to their premises for the program manager's inspection of the well, water supply and wastewater systems, especially if it meant entering a basement or less frequented area. It became necessary to accept the veracity of participants' statements in lieu of more technical observations to ensure enrollment, filter holder maintenance and sampling accessibility. Unfortunately, this compromise may have led to assumptions on the part of the program manager that may not necessarily be represented by fact. For example, the significant role of cellulosic sediment filters in optical brightener adsorption was delayed because of limited access and building occupants' lack of knowledge of their water supply plumbing. Wherever feasible, followup site visits were accompanied by additional questioning and observations to address certain facts that may still have been in doubt.

Laundry product usage became moot early in the project when it was determined that almost all detergents and other laundry products contain mixtures of both chlorine bleach-resistant and non-resistant optical brighteners (0.1 to 2 percent by weight) regardless of "dye-free" assertions on packaging. Rather, the appropriate questions regarded whether any laundry cleaning was done in the building and where the wastewater was discharged, as well as what neighbors were doing with their laundry wastes. In particular, it has become commonly accepted practice, albeit in violation of State and local regulations, to discharge laundry wastes to interior dry wells and sumps and exterior drainage ditches and closed depressions to relieve a malfunctioning or failed sewage system. The absence of conventional solids retention and soil treatment and the proximity to wells are significant concerns.

A variety of liquid and solid laundry products were purchased after determining their market share in the upper Midwest region. Reference samples of two of the most common optical brightener derivative groups were obtained from Ciba-Geigy [Tinopal (trademark) CBS-X (ASTM DSBP-1, a derivative of distyrylbiphenyl, Lot No. 34918038) and 5BM-GX (ASTM DASC-4, a derivative of cyanuric chloride, diamino-stilbene, Lot No. 1009) respectively]. Cotton pads were exposed to dilute solutions of the laundry products and the reference samples and then were analyzed with the scanning spectrofluorophotometer for characteristic excitation, emission and



synchronous spectra. With little variation from product to product, an optimum peak emission of 440 nm was confirmed, as well as several smaller secondary peaks.

Toilet tank reservoirs continued to be the location-of-choice for immersion filter holders containing cotton and other filter media. The tanks protected the filter holders from disturbances and light (photodecay of optical brighteners is significant). However, cleaning and disinfecting toilet tank reservoirs were not done because of the prevalence of chlorine bleach-resistant optical brighteners and the decision to maintain the status quo practices of building occupants and, therefore, minimize the introduction of new and unknown variables. Observations over the project period revealed that many tanks were colonized by bacteria (primarily iron oxidizing and sulfur reducing species) and molds which spread by the airborne drift of capsules and spores. The longer that the period of filter holder immersion was, the more likely that some filter media would support bacterial growth (cotton and activated carbon but not polysulfone/polyethersulfone filter membranes) which contributed to the masking of adsorbent surfaces and diminuation of optical brightener adsorbence.

Immersion filter holder design, fabrication, filter media contents and placement evolved over time with the recovery of older, exposed immersion filter holders (IFH). Although the IFH concept has been used by other workers in the field of fluorescent dye tracing, the aspect of long-term placement for the potential adsoption of ambient, low concentrations of various fluorescent dyes rather than larger injected dye quantities was untested. The following details the problems that occurred and the resolutions that were developed:

1. The immersion filter holder material, itself, must be resistant to physical forces applied to it, biologically and chemically inert, non-adsorbing, permeable to water but exclusive of larger solid matter, economical and readily available. Black, very fine-mesh fiberglas window screening was selected [e.g., steel screening corroded, aluminum screening lacked strength and was costly, and cellulose milk socks (used for immersion holders for fluorescent dye tracing) contained optical brighteners];
2. Depending upon the type and amount of filter media contained, the IFH could be large (approximately 4 inches by 6 inches), intermediate (about 3.5 inches by 5 inches) or small (3 inches by 4 inches or 3 inches square). The final, approved design called for them to be folded twice for strength and gross filtration from a larger, rectangular sheet of triple-rinsed (triple deionized distilled water), black fiberglas window screening;
3. Although many methods were used to seal the fiberglas to create pockets for the filter media, only two were successful. Solvent welding the fiberglas was strong but brittle, more costly, time consuming and used hazardous materials. Stapling proved to be the best method even though the individual staples would often rust and occasionally open. The rusting of staples was generally no more of a problem than the oxidized iron prevalent in the susceptible water supply systems already. Increasing the number of staples resolved the latter problem;
4. The means of IFH attachment to the toilet tank's standpipe was a problem at first as wire had been used. In aggressive water, the steel would sometimes corrode through releasing the filter holder. A number of filter holders were thrown away by building occupants as a result. The use of plastic tywrap of various lengths resolved the problem although it provided less flexibility in IFH placement modes;
5. In spring ponds and runs, several different problems threatened to minimize the number of recoverable IFH's as follows:
    a. Because of widely variable discharge rates, the IFH and its position, attachment and contents were subject to substantial [illegible]ement, physical

abrasion and erosion of the contents. Monofilament fishing line was found to be excellent in securing IFH's to above water surface reference points in most cases. However, no satisfactory alternative was found for holder material;

b. Cotton pads were severely eroded, and frequently little or nothing remained after variable exposure periods. Investigation revealed the following causes which have yet to be resolved:

i. Physical loosening and removal of the cotton fibers by turbulent flow, suspended and streambed load materials and repetitive pounding against rocks;

ii. Bacterial and fungal colonization of the cotton fibers as an organic substrate and nutritive source; and

iii. Consumption of cotton fibers or grazing of their surface by macroinvertebrates (e.g., sideswimmers were observed grazing on cotton fibers in spring ponds and runs);

c. Masking of IFH or contents by detritus, precipitates and sediment.

Another aspect of optical brightener sorption that was recognized but difficult to overcome is the effect of temperature on adsorption rate. While laboratory trials were conducted at sample temperatures of 20 to 25 degrees Celcius, average groundwater temperatures of 10 degrees Celcius in southeastern Minnesota appear to slow adsorption rates consequently requiring extended exposure time to achieve similar results and, thereby, increasing the likelihood of masking. Anecdotedly, two sites (1009 and 1081) had hot water plumbed to the toilets to prevent condensation drips, and optical brightener sorption appears to have been enhanced. Finally, Ciba-Geigy's Tinopal (trademark) optical brighteners have a wide range of optimum adsorption temperatures (15 to 50 degrees Celcius), all of which are warmer than the groundwaters sampled in the study.

Due to initial problems with very low level optical brightener detection, the program manager and University of Minnesota colleagues contemplated using caffiene and related organic compounds as surrogates for optical brighteners since they too have waste and wastewater as their primary source. Literature reviews were conducted, and researchers were contacted for specific methodologies. However, the application proved to be very elaborate requiring advanced liquid chromatographic techniques and costly to set up and would have required an amendment to the project's approved research plan. Therefore, it was abandoned.

The serendipitous discovery that polyethersulfone and polysulfone membrane filters preferentially sorb optical brighteners simultaneously offered both important research directions and an overextension of limited resources. While the decision to explore the filter media proved successful, it also delayed or diminished other aspects of the project. Some of those delays are apparent in this final report as data analysis is incomplete and will have to be updated in August, 1995.

Originally, contracts with registered environmental laboratories were considered. Because the project spanned a biennium and it was unknown which of the reviewed laboratories would be selected, it was determined that more informal, negotiated prices for purchased services would allow flexibility should laboratory performance or costs become issues. As it turned out, this was a good choice and allowed continued bargaining to secure reasonable prices for the laboratory work. The majority of the environmental laboratory work was performed by the Olmsted County Health Department's Environmental Laboratory in Rochester and the Minnesota



Valley Testing Laboratories in New Ulm. No other laboratories could offer similar laboratory services at such low costs.

Additionally, water sample geochemistry was split between field analyses by the program manager (those parameters subject to immediate, significant changes) and more sophisticated instrumental analyses by the University of Minnesota's Hydrogeochemistry Laboratory. A hidden benefit to this approach was the analysis of same parameter by different laboratories allowing for expanded quality assurance tracking in some cases. These will be reviewed upon completion of the project's overall data analysis.

Also, late in the project period, the program manager determined that ammonia and ammonium were being poorly recovered in samples because of the length of time between sample collection and analysis. With the purchase of a portable ammonia and ammonium selective ion electrode and meter, it is believed that the highly volatile parameters were measured more accurately than and nearly as precisely as the same laboratory-based methodology. However, TKN (total Kjeldahl nitrogen) was not performed because of the digestion steps (difficult in the field) and high method detection limit (approximately 1.0 mg N/L), the latter of which limits its utility in all but the most contaminated site assessments where concentrations of TKN would likely be detectable at and above 1.0 mg N/L.

The objective to ascertain if optical brighteners interfere with the detection of chemically related triazine herbicides, specifically atrazine, by causing false positive results when atrazine is actually below method detection limits, is as yet inconclusive due to incomplete data at the time of this report. Aatrex 9-0, a trademarked, dry, flowable atrazine product of Ciba-Geigy (85.5 percent pure atrazine, 4.5 percent atrazine derivatives and 10.0 percent inert ingredients), was obtained from Farmers Mill and Elevator (courtesy of Joe Auge, President), Castle Rock, Minnesota (EPA Registration No. 100-585, ID 58430; Lot No. SG 411011, BA 19-WPS; Dated 11-94), and is similar to atrazine products currently in use for most of the southeastern Minnesota area.

Experiments focused on two approved, common methods for atrazine analysis, namely the immunoassay and the gas chromatographic pesticide residue assay methods utilizing a nitrogen-phosphorous detector. Advanced assay methods which are capable of detecting atrazine residues and its degraded products, namely deethylatrazine, deisopropylatrazine and hydoxyatrazine, were not utilized because they are not ordinarily performed by commercial environmental laboratories, because of inherent extraction and analytical difficulties and because of turnaround time for results. However, should cyanuric chloride, diaminostilbene optical brighteners be detected as or interfere with the former common test methods, then the latter assay methods would be appropriate to better discriminate the nature of the chemicals responsible for the false positive detection or analytical interference.

First, likely sites with atrazine positive results (albeit very low concentrations) were sampled in replicate with one serving as the atrazine background sample and the other utilizing the standard addition technique to place a known quantity of optical brightener [Tinopal (Ciba-Geigy trademark) 5BM-GX] to determine if the method used would recover the latter as well. Additionally, the reference sample of Aatrex 9-0 (trademark, Ciba Geigy) was solubilized and exposed to cotton, as well as an Acrodisc PF (trademark, Gelman Sciences) 25-mm diameter, syringe filter to determine if atrazine, its derivatives, carriers or "inert" materials fluoresce in the range of optical brighteners.

A.3.b. Progress:

A fluorometric detection system has been designed and tested for optical brighteners (also known as fabric whitening agents or FWA's) which are synthetic organic blue dyes that fluoresce bluish-white upon exposure to ultraviolet light and that are utilized in laundry products and consequently discharged with domestic wastewater to sewage treatment systems. The detection system is comprised of several types of filter holders with adsorbent, selective media, a solid and liquid phase scanning spectrofluorophotometer and computer software-driven data manipulation for comprehensive and objective analysis. In this and companion studies to date, the system has been used successfully in detecting treated effluent from municipal wastewater treatment facilities (WWTF) and their downstream receiving waters, treated and untreated on-site sewage treatment system effluent and treatment area infiltration and percolation to groundwater, surface streams and groundwaters. (Attachments 1 and 2.)

The detectors included immersion, in-line and syringe filter holders which contained a variety of adsorbent filter media (untreated cotton pads, activated carbon and polysulfone/polyethersulfone membrane filters) which were respectively exposed to passive flows (long-term immersion) and active continuous (short-term in-line) and discontinuous (short-term syringe) flows. The immersion filter holders were placed in the tank reservoirs of the most used toilets in residences and businesses, spring ponds and runs, treated municipal WWTF outfalls, on-site sewage treatment system effluents and surface streams. In-line filters were attached to untreated, cold water taps for continuous sampling, and syringe filters with polyethersulfone membranes were used to discretely sample drinking water, treated wastewater effluent and surface streams.

The untreated cotton was selective for optical brighteners provided blank pads were scanned for trace optical brighteners (certain manufacturers utilize recycled cotton which may have been previously brightened) and for native fluorescence of cotton (optimum emission wavelength of 415 nm) which could interfere with low level optical brightener detection (optimum peak emission wavelength of 440 nm). Concern for fluorescent dissolved organic carbon compound (FDOC) interference (emission wavelengths of 200 to 450 nm), which plagues aqueous sample testing for very low concentration optical brighteners (including naturally occurring humic and fulvic acid derivatives), was allayed in a comparative study with activated carbon which, unlike cotton, is an indiscriminate adsorber of organic chemicals including FDOC's.

However, cotton's utility is impacted by the masking of fibers by precipitates, sediment and bacterial colonization and by physical fiber erosion, microbial degradation and other fiber destruction or removal. Since immersion is reliant on long-term cotton exposure to improve the chances of optical brightener sorption, the primary drawback to this method is the masking, erosion, degradation or destruction of cotton fibers during an optimum exposure period which may preclude sorption or remove already brightened fibers yielding false negative results.

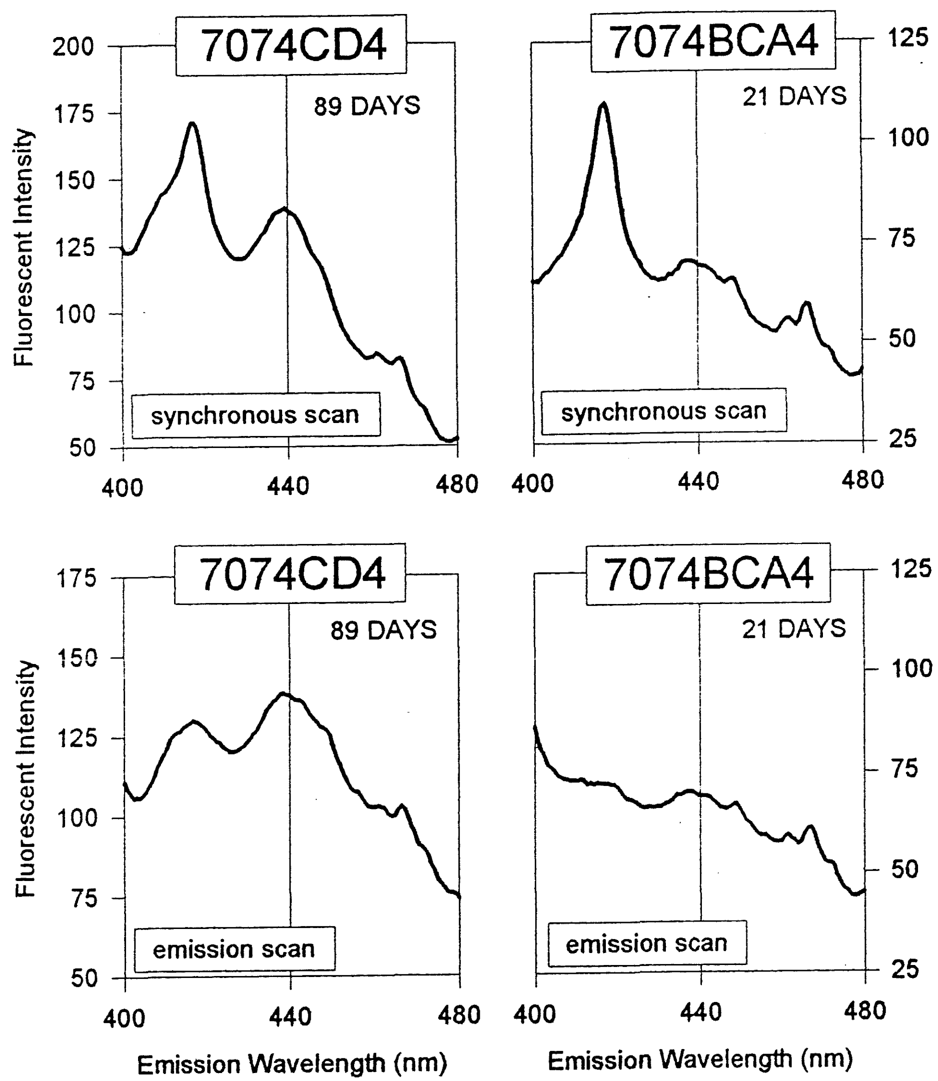


Therefore, untreated cotton is a conservative and highly selective adsorber of optical brighteners, but it can only be used as a qualitative detection method indicating presence or absence of optical brighteners due to the aforementioned conditions. In a passive exposure, immersion environment, the shorter that the exposure time is with respect to a positive result, then the greater is the likelihood that the optical brightener concentration will be high enough to reveal a positive, semi-quantitative result utilizing the in-line or syringe filter sampling method. The optimum exposure period for cotton immersion filter holders appears to be about 4 to 12 weeks but is highly dependent on other conditions (optical brightener concentration, number and volume of flushes, water temperature, filter masking, etc.).

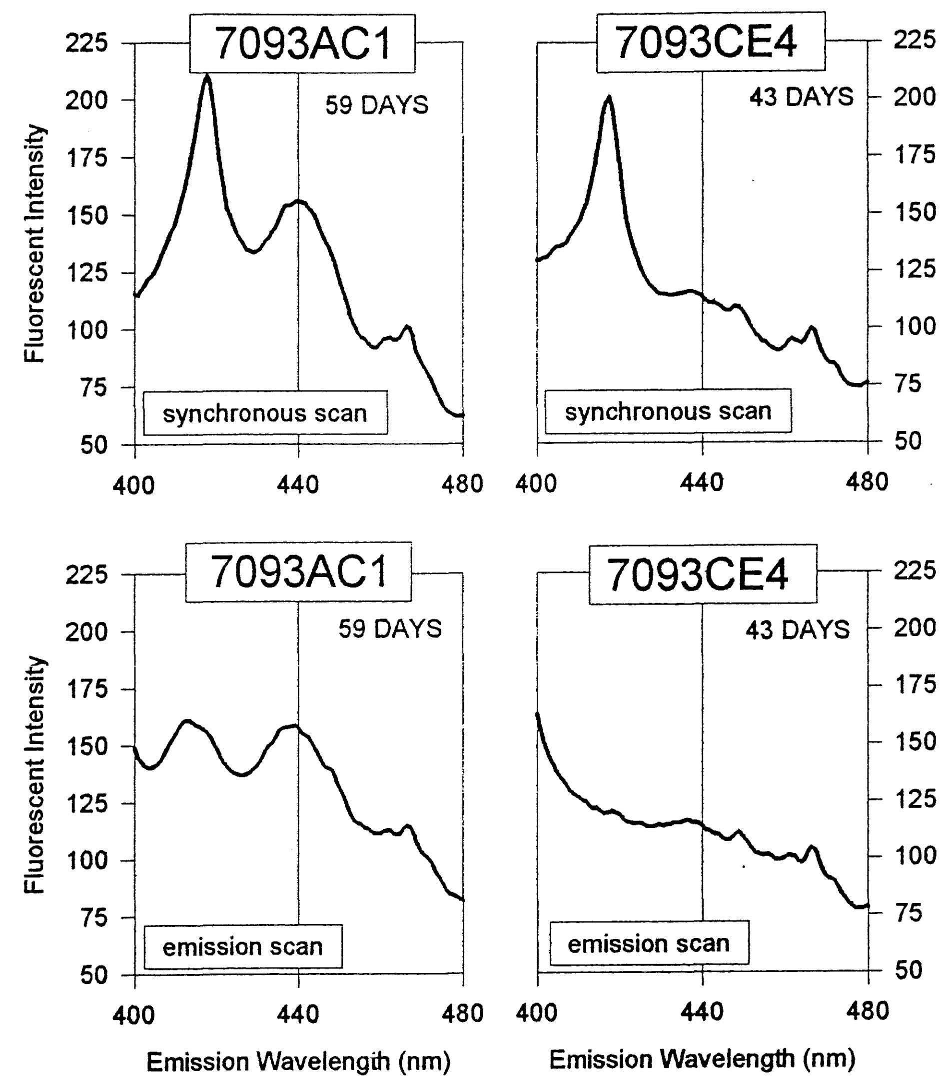
Utilizing immersion and in-line filter holders for cotton exposure to sample potential optical brightener-contaminated groundwaters, a number of experiments were undertaken to logically verify the main hypotheses. They are as follows:

1. Multiple cotton pads were placed in each filter holder with pads tightly facing back to back. The exposed sides were consistently brightened in contrast to the covered sides which were, in contrast, unbrightened;
2. The length of time exposed generally compared favorably with increased brightening (range 4 to 12 weeks) and then levelled off or declined thereafter due to saturation, masking or erosion. For immersion filter holders, only estimates of the average number of flushes per day could be obtained, but time and volume may yield a more valid correlation with optical brightener intensity (refer to Attachment 1):
    a. For the same site utilizing immersion filter holders, the observed cotton optical brightener fluorescence intensity was significantly greater [e.g., **Pleasant Grove, Olmsted County**, site 7074 data compares emission and synchronous scans from 21 and 89 days immersion time];
    b. A bit more equivocal, for example, are results from **Marion, Olmsted County** site 7093 which show a significant difference in fluorescence intensity but little difference in immersion time (43 versus 59 days). The difference may be explained by the variability in optical brightener concentration in the very shallow groundwater (the masking of cotton was minimal at this site);
    c. Utilizing long-term immersion versus short-term in-line filter holders, the observed fluorescence intensity was significantly greater as well [e.g., **Hampton, Dakota County**, site 1002 data compares scans from continuous 2-day in-line filtration to 64-day immersion filtration];
3. Generally, wells completed in the first aquifer which may be impacted by sewage contamination yielded positive optical brightener detections compared with nearby deep wells with negative optical brightener detections because of dispersion and dilution, protective casing, cement grouting or other factors:
    a. For example, comparing a shallow, upgradient well (**Vasa, Goodhue County**, site 4040, completed in the Prairie du Chien dolostone), which was positive for optical brighteners, with a deep, downgradient well (Vasa, site 4059, completed in the underlying Jordan sandstone), which was negative, verifies the susceptibility of the former well and confirms the appropriateness of one or more wellhead protection factors that minimize contaminant transport even though no regional aquitard is present and the Prairie du Chien-Jordan is considered regionally as a single aquifer;
    b. Within the same aquifer (in this example, the Galena formation which is the lowest unit of the Upper Carbonate Rock Aquifer of southeastern Minnesota) and especially in a known karst aquifer system, the local groundwater gradient was reflected in the optical brightener results. At **Fairview, Fillmore County**, the upgradient well site [illegible]7 had significantly

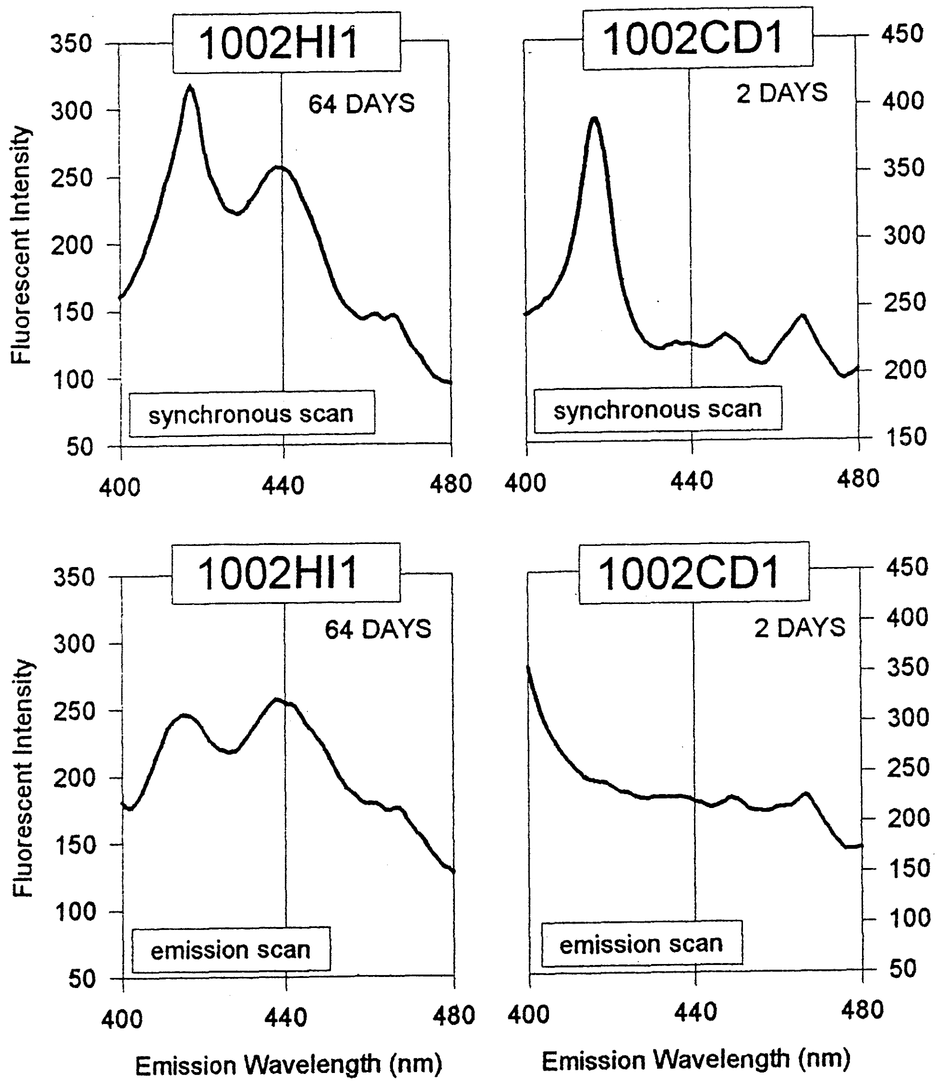
# Pleasant Grove



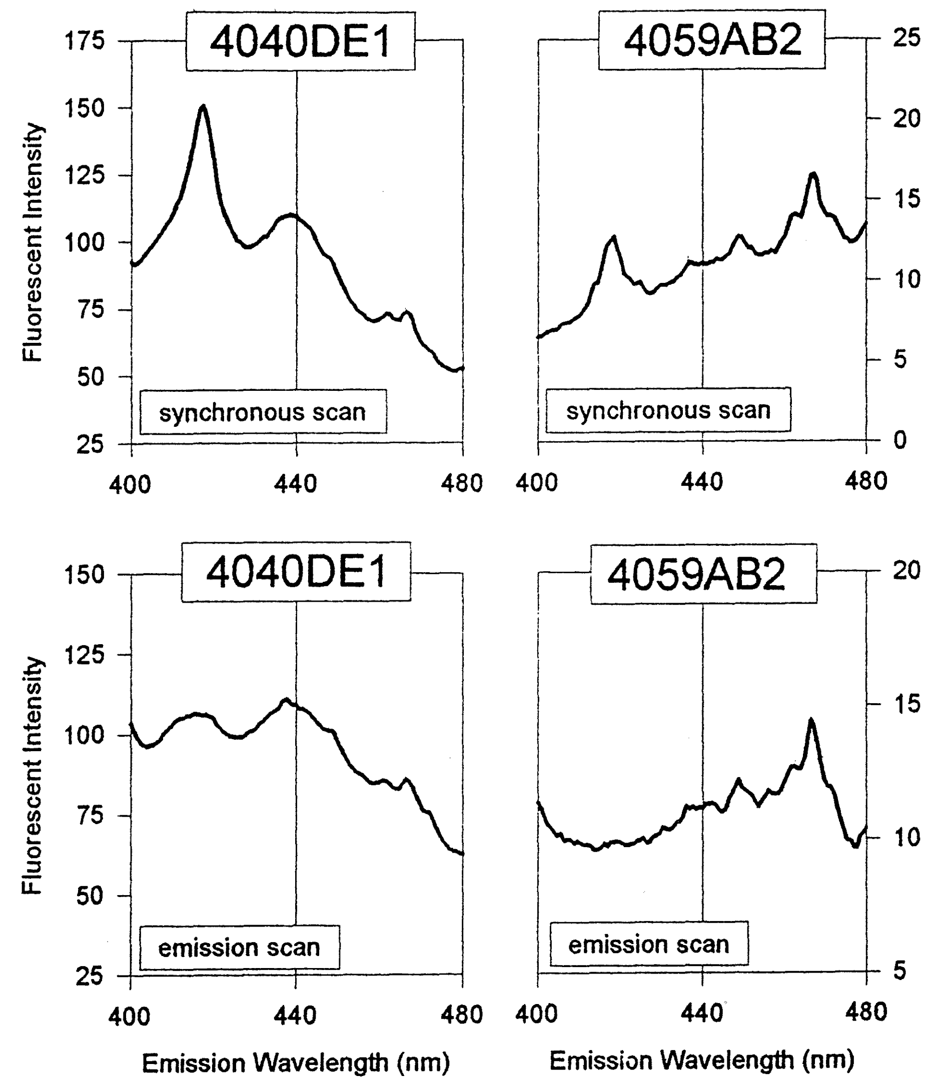

# Marion



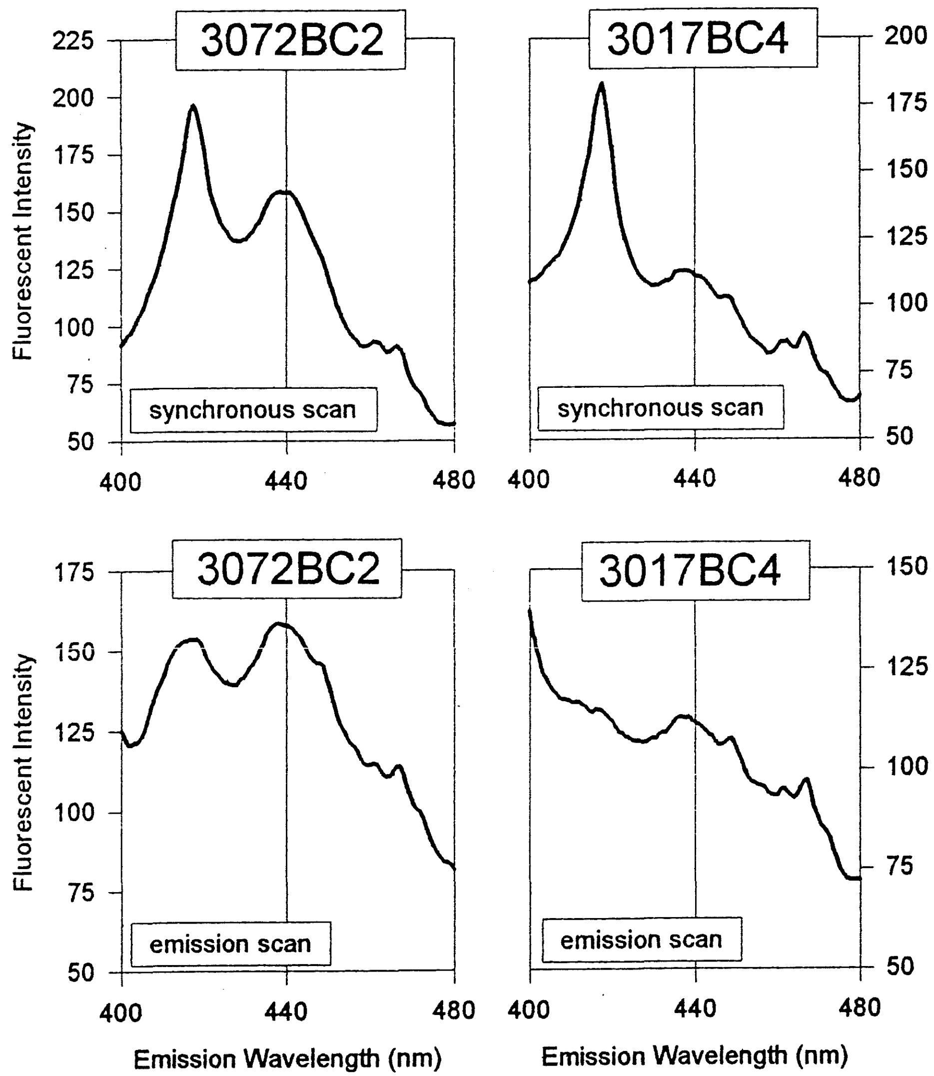
## Hampton



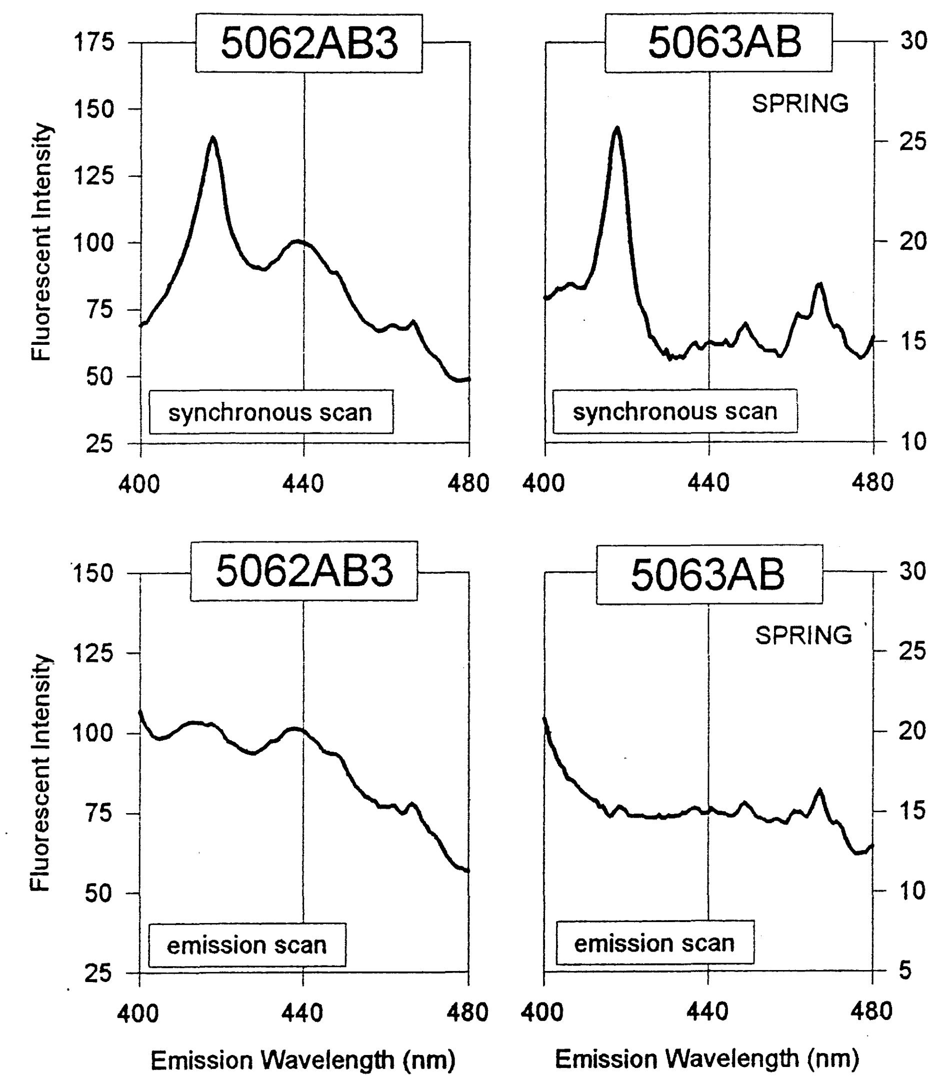

## Vasa



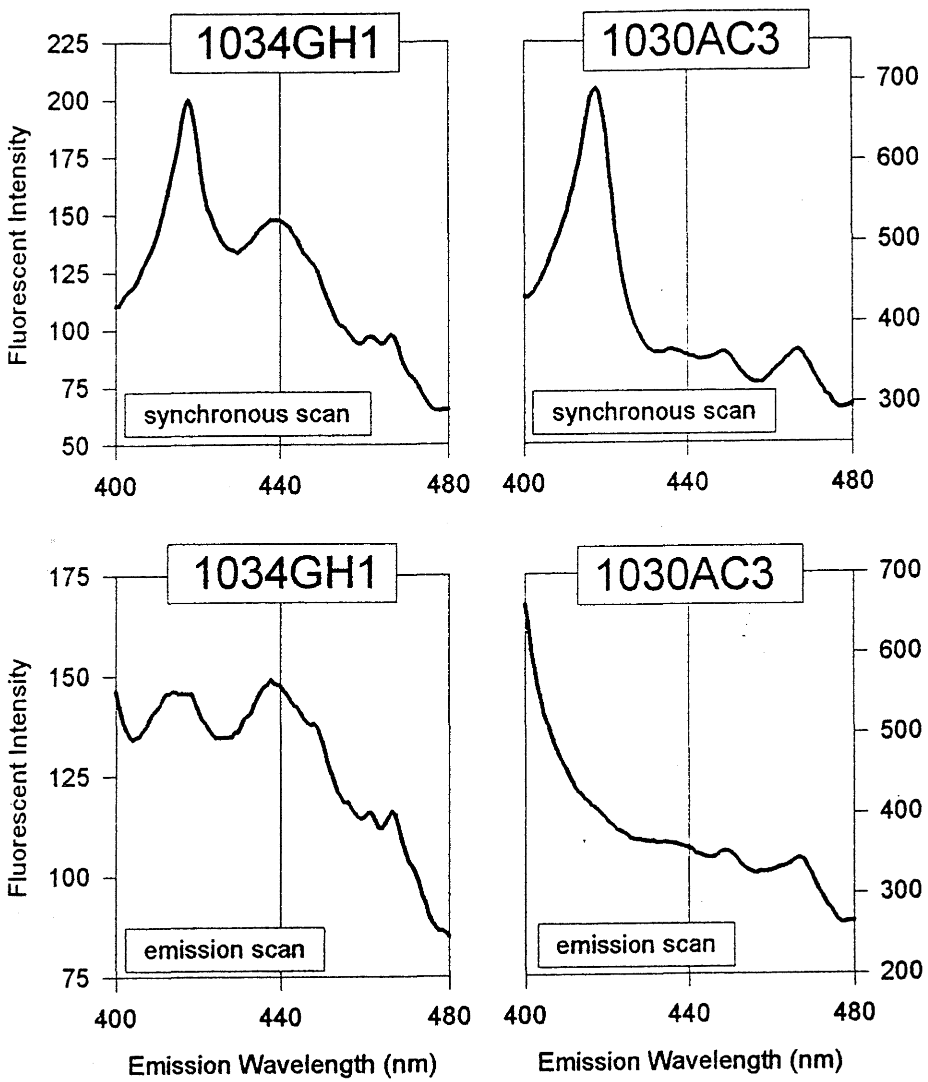
## Fairview



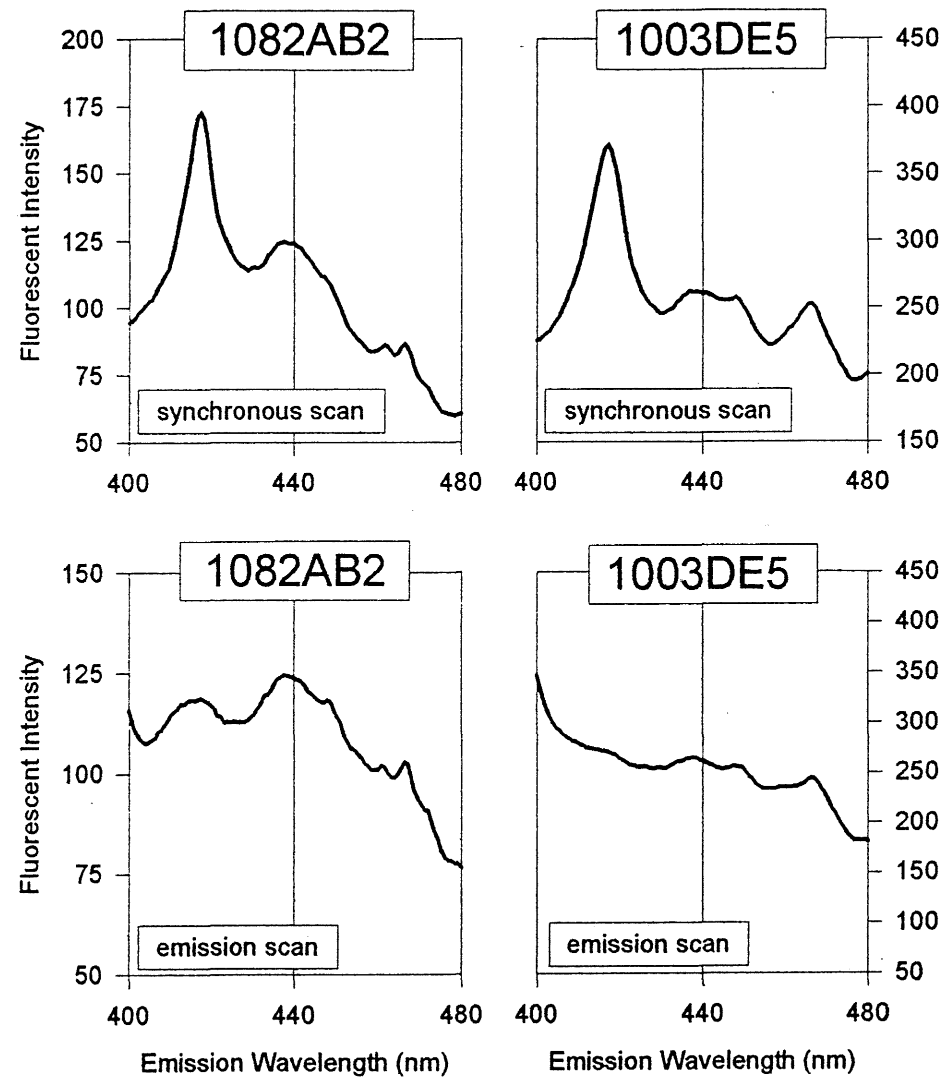

## Trollskogen



# Coates




# Farmington



less fluoresence intensity than the downgradient well site 3072 and the sanitary test data corroborated the results;

4. An urban environment without private wells and sewage systems was selected in which the older city wells were not cased and grouted through the shallow upper aquifer and laundry and solvent cleaning wastes allegedly migrated through the regional aquitard (Decorah shale) via the unprotected well. In this case, the shallow groundwater some distance from the center of town was negative for optical brighteners while the deeper well was positive for both optical brighteners and cleaning solvent. **Spring Grove, Houston County**, site 5062 at Trollskogen Park, which is supplied by one of the city's contaminated, deeper wells, was positive for optical brighteners, whereas cotton samples from nearby site 5063, Trollskogen Park Springs, which are a number of small Galena-Decorah contact springs and seeps, were negative. This demonstrates how optical brighteners could be effectively and economically used to confirm the source of a related contaminant;

5. To test the effectiveness of cellulosic sediment filters to remove optical brighteners, comparisons were made both before and after the sediment filters were removed. In several cases, unbeknownst to the owners, they had switched from cellulosic (e.g., pleated paper) to non-cellulosic (e.g., polypropylene string) materials with the resulting breakthrough of optical brighteners in the latter case:

    a. At **Coates, Dakota County**, site 1030, a pleated paper filter has treated the entire household water for iron and sand sediments, and all of the cotton samples scanned were negative save one small positive result. In comparison, site 1034's well is virtually the same in depth and construction, but more upgradient, but no sediment filter or other treatment has been used. Consequently, all samples have been positive for optical brighteners;

    b. At **Farmington, Dakota County**, site 1003 was utilizing a pleated paper sediment filter and, consequently, samples for optical brighteners remained negative until the owner began installing newer polypropylene string sediment filter cartridges, the hardware store had discontinued carrying the pleated paper cartridges and began stocking polypropylene string cartridges without his knowledge. However, downgradient well site 1082 with a drivepoint completed to the same depth in the same shallow aquifer was always positive for optical brighteners.

Although activated carbon was primarily used in the project as a means of monitoring FDOC concentration and the potential of optical brightener interference, its utility in sorbing other fluorescent, organic dyes contributed by other pollution sources is known. Similar to low level optical brightener detection, the advent of scanning spectrofluorophotometry and its computer-aided data analysis was crucial in the very low level detection of fluorescein, rhodamine and eosin. However, adsorbed dyes must first be elutriated from the carbon by a strong base in a water-based solvent system (e.g., sodium hydroxide in propanol-water solution) and then analyzed. Work continues on improving elutriant solution chemistry to optimize the recovery of dyes from carbon and minimize the quenching of their fluorescent properties. Such dye detections are indicators of the contamination of water, and their presence substantiates the detection of optical brighteners. Therefore, the passive immersion detection system should include activated carbon, as well as untreated cotton.

Concommitant with and supported by the project's methodologic preparations, the graduate student, Steffan Fay, applied to the National Ground Water Association for a research grant to study the movement and retardation of optical brighteners



through a sand column. Awarded a grant of $1000, he ran a mixture of dyes, including optical brighteners, dissolved in pristine, uncontaminated groundwater through a column packed with Rosemount outwash sands (Quaternary: Wisconsinan) and recovered them with continous scanning spectrofluorometry. The recoveries of eosin and, in particular, optical brighteners were very poor leading to speculation that their sorption on sand was significantly higher than found in earlier studies. However, the meticulous search for an answer was rewarded in the serendipitous discovery that the prefilter [Gelman Acrodisc PF (trademark)] to the scanning spectrofluorophotometer's flowthrough cuvette was sorbing some of the eosin and most of the optical brighteners. Further study demonstrated that the 25-mm diameter membrane filters, in particular the 0.8 micron pore filter, comprised of polyethersulfone accounted for nearly all of the optical brightener adsorption.

Subsequently, laboratory and field experimentation with polyethersulfone and polysulfone membrane filters [Gelman Sciences trademarks: Acrodisc PF, Acrodisc, Supor, Tuffryn, BioTrace and UltraBind] was conducted in all three sampling modes, namely immersion, in-line and syringe filter holders. Although data analysis is incomplete, it appears that the immersion sampling mode for polysulfone and polyethersulfone is ineffective because of passive adsorption to only the filter surface area rather than active adsorption with volume flow through the membrane. The in-line sampling mode received the least number of trials with limited results and will be continued with very low concentration standard additions of optical brighteners to determine semi-qualitative recoveries of optical brighteners when paired and exposed with and without standard additions. Blanks of membrane filters, triple deionized distilled water and optical brightener standard serial dilutions will be run.

The syringe filter sampling mode utilizing the Acrodisc PF (Gelman Sciences trade-mark) appeared to have significant success when compared to all other membrane filters and sampling modes. The filter is unique in that it has two polyethersulfone membranes, a 0.8-micron pore prefilter and a 0.2-micron pore final filter, in tandem with a separation between the two. It is surmised that the sulfone component of the membrane may enhance the chemical sorption of the sulfonated optical brighteners, but there is as of yet no conclusive evidence either way for chemical or physical adsorption.

The difference in sorption efficiency of various membrane filters could be explained by the filtering of very finely divided solids which include undissolved optical brighteners [solubilities vary for each dye and range from 2.5% at 25 C for Tinopal CBS-X to 1.5% at 50 C for Tinopal 5BM-GX (Tinopal is a Ciba-Geigy trademark)]. Such solids, however, are more likely to be removed by sewage treatment biomats and aquifer materials and thus would limit the syringe filters' use in groundwater investigations as opposed to wastewater investigations where their utility has already been proven effective. Using an 1.0-micron pore glass prefilter upstream of the Acrodisc PF did not alter the results although smaller pore-sized glass filter sizes were not examined yet. Other syringe filter combinations are being evaluated to determine if a difference in filter material, pore-size, single versus tandem filters and other factors can account for optical brightener adsorption efficiency.

Markedly increased pressure or vacuum [starting at about 20 and possibly exceeding 120 pounds per square inch (psi)] is required to pump 2 to 4 liters of sample through the Acrodisc PF syringe filter because of filter clogging even with the use of multiple1.0-micron pore glass prefilters. This was difficult to achieve in the field using a variety of peristaltic and vacuum pumps. Tedious, manual pumping was successfully used to filter the minimum volume needed and simultaneously guard against premature syringe filter failure or hose detachment or rupture. Surprisingly, syringe filters rated at 40 psi held up remarkably well although some burst at the equatorial seam at higher pressures.

With respect to tandem filters (e.g., the Acrodisc PF), it is possible that the differential flow through the two filters causes backpressure and may slightly elevate temperatures due to flow resistance. The 0.8-micron pore prefilter preferentially sorbs almost all of the optical brighteners, and the 0.2-micron final filter sorbs virtually none. If filter adsorption were governed solely by the chemistry of dissolved optical brighteners and the filter media, one would presume that both the large and small pore filters should retain detectable optical brighteners.

Correlation of positive detections of optical brighteners with the microbiologic and physicochemical attributes of the water supply is mixed depending upon the parameter of interest. Although data analysis is still incomplete and will be updated in the August, 1995, revision, it appears overall that chloride concentrations above regional background levels (< 10 mg/L) are the most sensitive indicators of sewage contamination of groundwaters considering their correlation with the presence of optical brighteners. However, chloride, by itself, is not a reliable sewage system contamination indicator as it has many potential sources (e.g., road salt).

Interestingly, Alhajjar, et al, 1990, in a study of the performance of central Wisconsin sewage treatment systems utilizing drivepoints for the sampling of shallow groundwater near the treatment areas, determined that chloride was the most significant sewage system indicator and dismissed optical brighteners as the least reliable indicators (however, they relied on dated, fluorometric techniques using aqueous sample analysis prone to FDOC interference) selected for analysis.

Correlations with the traditional sanitary indicators, namely total coliform bacteria and nitrate-nitrogen, were not particularly significant. However, numbers of studies (Bitton and Gerba, 1984) have determined that coliform bacteria are readily strained by microporous, semipermeable soils and consequently poor survivors outside of their human and animal hosts. Likewise, nitrate is but one form of nitrogen and requires aeration, favorable oxidative chemistry and soil microbiology. Since sewage nitrogen is primarily in the reduced forms of inorganic ammonia and organic nitrogen compounds, the absence of nitrate in a drinking water supply does not necessarily imply it is as safe as environmental folklore would have one believe. Certainly, the presence of ammonia or ammonium ions, soluble organic nitrogen and/or nitrite should be cause to examine the water supply more closely as they suggest the presence of a close source of nitrogen contamination (or possibly colonization by denitrifying bacteria).

Another, relatively independent, test of the reliability of the fluorometric detection of FWA's is its correlation with hydrogeological position with respect to well depth and intake, groundwater flow and direction and contamination sources. Considering the plausibility for the contamination of the shallow to intermediate depth aquifers of interest, there appears to be corroboration for that hypothesis in most of the twenty site areas studied. Additional evaluation will be available when data analysis is completed.



The first project-related paper, entitled "Optical Brighteners as Indicators of Septic System Pollution in Water Table Aquifers of Southeastern Minnesota", was co-authored by Steffan Fay, his advisor, Professor E. Calvin Alexander, and the program manager. It was presented orally by Steffan Fay to the Annual Conference of the American Water Resources Association held in Chicago, Illinois, on November 8, 1994, and is published in abstract form in the conference's proceedings. The paper summarized the current methodology developed, and it focused on sampling and investigations in the villages of Castle Rock, Coates and Empire City in Dakota County and the village of Vasa in Goodhue County.

Two project-related papers were presented at "Solutions '95", the 26th International Congress of the International Association of Hydrogeologists which was held in Edmonton, Alberta, Canada, on June 4-10, 1995. The papers are included as Attachments 2 and 3 to this final report and were published in the Congress Proceedings and are available on CD-ROM. The first paper (Attachment 2), entitled "Optical Brighteners: Sorption Behavior, Detection, Septic System Tracer Applications", introduces the field and laboratory methods developed for the spectrofluorophotometric analysis of optical brighteners. The second paper (Attachment 3), entitled "Optical Brightrener Screening for Sewage Contamination of Water Table Aquifers in Southeastern Minnesota, USA", details the preliminary fieldwork and results for the communities of Castle Rock, Coates, Empire City and Vasa.

B. Title of Objective: Evaluate monitoring data and information.

B.1. Activity: Organize, review, maintain datafiles, statistically analyze and evaluate data and information collected. Submit draft reports for peer review. Conclude study and submit final report.

B.1.a. Context within the project: During and upon the conclusion of the field and laboratory data acquisition phase of the study, all information and data will be organized, reviewed and, wherever appropriate, entered into datafiles for ongoing evaluation, updating and statistical treatment. Experts in groundwater science, agricultural chemistry and related study areas will be consulted to critique work plans, data and information, and conclusions.

B.1.b. Methods: All relevant information and data will be collected, organized and stored in hard files and computer database files as the study progresses. Datafiles utilizing Paradox and Foxpro database management software will be maintained for frequent review and analysis. Statistical treatment of appropriate data will be accomplished utilizing several formats and models available on SPSS+ software or its equivalent. Harvard Graphics and other software will be used for rendering diagrammetric and graphic data. Specific data for sites in Dakota County will be transferred to the County's ARC/INFO Geographic Information System (GIS), and similar data for other counties may be transferred to similar GIS programs at the state or appropriate county level.

B.2.c. Materials: This objective is accomplished utilizing existing hard file storage and computer databases and software (Paradox, Foxpro, Harvard Graphics, ARC/INFO GIS, ARC/VIEW, etc.).

B.1.d. Budget: $25,000.
Estimated Balance: $6,000

| B.1.e. Timeline: | 7/93 | 1/94 | 6/94 | 1/95 | 6/95 |
|---|---|---|---|---|---|
| Classify/enter datafiles | | | ************************************ | | |
| Conduct statistical calc | | | ***************************************** | | |
| Create ARC/INFO GIS | | | | *********************** | |
| Complete study evaluation | | | | | ***** |

B.2. Status:

B.2.a. Problems and Progress:

As previously reported, the project manager determined that Microsoft Office Plus for Windows was the most practical software package for the multiple computer tasks required by the project, and it was recently supported by the Dakota County Data Processing Department to integrate it with the existing Foxpro software-based database management programs that were recently upgraded. In particular, the County's Geographic Information System (GIS) which is written in ARC/INFO and ARC/VIEW will be accessible via Foxpro and Microsoft Office Plus's "Access", a user friendly relational database management system which is compatible. The design will be similar to and compatible with the information management system for the LMIC. However, development, as well as data entry, is still underway. An update will be submitted in August, 1995.

## V. Evaluation

For the FY94-95 biennium, the study may be evaluated by: 1.) The extent and completion of field work in the nine-county area; 2.) The completion of laboratory analyses of optical brighteners, background parameters, pollution indicators and contaminants of concern or interest (e.g., nitrate-nitrogen and triazine herbicides); and 3.) The ongoing analysis and completed evaluation of study information and data.

In the long-term, the study may be evaluated by its utility in aiding environmental science practitioners (regulatory, academic and industry) with their understanding and evaluation of domestic sewage contamination of groundwaters. If successful in discovering that optical brighteners may be implicated in the false positive detections of triazine herbicides in groundwaters, the study would resolve some problems previously noted in other investigations.



## VI. Context Within Field

To date, the specific impact of domestic sewage on the contamination of groundwaters in Minnesota and elsewhere is unknown. Due to the ubiquity of nitrogen (e.g., nitrates) and other sewage parameters in the environment, isotopic nitrogen analyses have been only marginally successful in identifying contamination sources in agricultural areas. However, such assays are cost-prohibitive and unavailable to the majority of workers and researchers.

The inability to identify nitrogen and other contaminant sources in impacted groundwaters makes it difficult to target the actual primary sources and affectuate remedies. In particular, owners of sewage systems in agricultural areas blame farmers for the elevated nitrates in their water supplies, and such a bias impedes regulators from adopting regulations and zoning ordinances where the sources of the contamination cannot be proven.

Regulators and researchers alike have noted the prevalence of triazine (especially, atrazine) herbicide residues in the groundwaters of agricultural areas. However, some researchers have noted positive detections of atrazine in areas where little or no atrazine had reportedly been used. Such potential false positive detections create difficulties in assessing the true extent and impact of triazine herbicide contamination of groundwaters. With the advent of state bans or restrictions on their use and the employment of best management practices where still permitted to be used, atrazine and other triazine herbicides may be unduly restricted in some environments where false positive tests are prevalent.

The study will focus on research needs in the above described areas with potentially significant results being immediately transferrable to the environmental practitioner and land owner. In particular, the study results, whether positive or negative, will be shared with the Minnesota Department of Agriculture and the University of Minnesota research staffs working on related legislative studies and initiatives.

## VII. Benefits

The study may be applicable to most of Minnesota and will benefit groundwater protection planning and implementation as domestic sewage systems and agricultural fertilizer and herbicide use are the two most significant non-point sources of contaminants recognized statewide. The utility of a passive, conservative tracer of domestic sewage contamination would be a useful tool for the environmental practitioner and researcher. They may be able to ascertain the approximate proportion of a common contaminant, such as nitrate, that is related to domestic sewage systems by determining optical brightener concentrations in groundwater. Depending upon the location and the aquifer, statistically significant regression analyses of nitrate-nitrogen (or another contaminant) concentration on optical brightener concentration may allow a reasonable interpretation of the impact of domestic sewage on drinking water supplies. In contrast, the unrelated concentration of nitrate (or another contaminant) may then be attributable to other non-domestic sewage sources. Such results may be used to target potential contamination sources more precisely focusing mitigative measures and other location-specific solutions (zoning, sewage system requirements, agricultural best management practices, etc.).

The use of a cotton detector for optical brightener screening of domestic sewage contaminants would be an effective, economic tool for the sanitary evaluation of drinking water supplies that presently rely upon only two sanitary parameters, namely total coliform bacteria and nitrate-nitrogen. It is known that acceptable results for either of those sanitary tests are possible even if the water supply is contaminated with domestic sewage because of several factors. If standard sanitary testing were to incorporate both specific conductance testing and optical brightener screening as well, there would be less chance of not identifying possible domestic sewage-contaminated water supplies. In the repertory of environmental health professionals, such minmum requirements for sanitary testing would help identify problems and prevent disease for an unprotected segment of individual water supply consumers.

Given the apparent prevalence of atrazine in the groundwaters of Minnesota, significant legislation, regulatory action and agricultural consumption has diminished or restricted its use. If the study determines that some of the false positive testing of atrazine or other triazine herbicides may have been the result of interferences from or alternatively false detections of optical brighteners, the research and corrective actions related to triazine herbicides may be improved and beneficial to all parties.

## VIII. Dissemination

During and after the field and laboratory phases of the study, peers in regulatory agencies and academic institutions will be kept apprised of interim and final results and evaluations to elicit critical review to improve the study and to transfer any substantive findings that may have immediate value requiring test replication for verification.

In addition, formal and informal dissemination to others working in the area, including zoning administrators, planners, water resource managers, county extension agents and water supply/treatment professionals, will be encouraged where the results may be put to practical use.

Depending upon the results and conclusions, the study's findings will be presented formally at local, state and national scientific meetings attended by peers in associated disciplines. Additionally, presentations and papers will be submitted for publication by peer-reviewed, professional journals to ensure a wide audience and promote related investigations to verify the results and conclusions of the research elsewhere.

The study data will be stored in Paradox and Foxpro datafiles, some transferred to the County's ARC/INFO GIS and otherwise available for sharing with related databases at the state and municipal level for beneficial use. The datafiles will be coordinated with the Land Management Information Center for statewide utilization through IGWIS and associated information management systems and databases as needed.

The importance of some of the possible findings of the study may lead to local and state regulatory changes, especially in the recognition of definitive methods for defining impacts from domestic sewage systems (land use zoning, individual sewage treatment system standards, well construction and sealing standards, safe drinking water standards, etc.) and the identification of false positive detections of triazine herbicides. The findings will be disseminated to state legislators and municipally elected officials as appropriate to any recommendations for changes to existing laws.



## IX. Time

The purview and intent of the study are to be completed within the FY94-95 biennium.

## X. Cooperation

Informal cooperation with peers in state and municipal regulatory agencies (e.g., Minnesota Department of Health, Minnesota Department of Agriculture, Minnesota Department of Natural Resources, Minnesota Pollution Control Agency, Minnesota Board of Water and Soil Resources, county public health departments and county planning and zoning offices), state academic institutions (University of Minnesota, Minnesota Extension Service and Winona State University) and others will be maintained throughout the study for coordination, guidance and critical review. No specific cooperators have been established.

## XI. Reporting Requirements

Semiannual status reports will be submitted not later than January 1, 1994, July 1, 1994, and January 1, 1995, and a final status report will not be submitted later than June 30, 1995.

## XII. Pertinent Literature


Alhajjar, B.J., G. Chesters, and J.M. Harkin, 1990, "Indicators of chemical pollution from septic systems", Ground Water, 28 (4): 559-568.

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Fay, Steffan R., E. Calvin Alexander, Jr., and Ronald C. Spong, 1994, "Optical brighteners as indicators of septic system pollution in water-table aquifers of southeastern Minnesota", Abstract in Proceedings of the American Water Resources Association, Conference, November 8, 1994, in Chicago, Illinois.

Fay, Steffan R., Ronald C. Spong, Scott C. Alexander and E. Calvin Alexander, Jr., 1995, "Optical brighteners: sorption behavior, detection, septic system tracer applications", Proceedings of the XXVI Congress of the International Association of Hydrogeologists, June 4-10, 1995, Edmonton, Alberta, Canada.

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## ATTACHMENT 1

## OPTICAL BRIGHTENER DETECTION METHODOLOGY AND RESULTS SUMMARY

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### 1.0 INTRODUCTION

This attachment describes methodologies developed for the detection of optical brighteners and presents a breakdown of the results of analysis of field samples. Field samples were grouped into batches based on submittal date. The summaries presented herein are based on the results of samples up to and including those in batch 38 (submitted June 2, 1995). The findings should therefore be considered somewhat preliminary, and will be revised and updated for the final project report.

### 2.0 METHODS

Optical brighteners can be detected using a spectrofluorophotometer. The spectroflorophotometer measures the light emitted from a sample at a specified wavelength or range of wavelengths when excited by light at another (shorter) wavelength or range of wavelengths. The fluorometer used was a Shimadzu RF5000U (Shimadzu Corporation, Kyoto, Japan).

The optical brightener detection methodologies employed in this study can be separated into two broad categories: detection in direct solution and detection on a solid medium. In the course of the study we have investigated optical brighteners in water, sorbed to unbrightened cotton, and sorbed to polyethersulfone filter media.

A microcomputer was used to control the fluorometer remotely and facilitate the electronic storage of fluorescence spectra. The analytical methodology developed during the course of the project entailed the use of three individual scans per sample, corresponding to the three scan modes of the fluorometer. The three scan types are as follows:

1) Synchronous scan. Excitation and emission wavelengths are varied by the fluorometer keeping a constant separation ($\Delta\lambda$).

2) Excitation scan. Emission wavelength is held at a specified value. Excitation wavelength is varied.

3) Emission scan. Excitation wavelength is held at a specified value. Emission wavelength is varied.

### 2.1 List of Materials

**2.1.1 Cotton Pads:**
Target brand.
Johnson & Johnson brand.

**2.1.2 Filter Media:**
Gelman Corporation. Ann Arbor, Michigan.

**2.1.3 Optical Brighteners:**
Tinopal 5BM-GX. Commercial grade. Batch #1009.
Ciba-Geigy Corporation. Greensboro, North Carolina.

Tinopal CBS-X. Commercial grade. Batch #34918038.
Ciba-Geigy Corporation. Greensboro, North Carolina.

**2.1.4 Laundry Detergents:**
Purex Ultra powder. Dial Corporation. Phoenix, Arizona.
All liquid. Lever Bros. New York, New York.
Woolite liquid. Reckitt & Colman. Wayne, New Jersey.
Cheer powder. Proctor & Gamble. Cincinnati, Ohio.
Tide Ultra powder. Proctor & Gamble. Cincinnati, Ohio.
Tide Ultra liquid. Proctor & Gamble. Cincinnati, Ohio.
Fab Ultra powder. Proctor & Gamble. Cincinnati, Ohio.

### 2.2 Sample Handling and Preparation

Direct samples were collected and stored in brown glass bottles. All samples were stored refrigerated in total darkness until analysis. Direct samples were analyzed in a 5 ml acrylic cuvette. Solid samples were analyzed in the fluorometer solid sample holder. Solid samples were left damp or dampened with deionized water prior to analysis to reduce scattering of excitation light.



## 3.0 RESULTS

### 3.1 Optimum Settings

The detection of optical brighteners requires the visual recognition of characteristic peaks in the fluorescent spectra of samples. Based on the results of analyses of laboratory prepared optical brightener standards and laundry detergents both in solution and sorbed to cotton, the following RF5000U fluorometer settings were found to be optimum for the detection of optical brighteners (and optical brighteners):

**3.1.1 Direct Solution**

| | |
|---|---|
| Sensitivity: | high |
| Band width: | 3 nm |
| Synchronous scan: | $\Delta\lambda$ = 95 nm, vary emission wavelength between 320 nm & 520 nm |
| Excitation scan: | Emission wavelength = 440 nm, vary excitation wavelength between 240 nm & 430 nm |
| Emission scan: | Excitation wavelength = 345 nm, vary emission wavelength between 355 nm & 570 nm |

The presence of optical brighteners is indicated by peaks at the following wavelengths:

| | |
|---|---|
| Synchronous scan: | 440 nm |
| Excitation scan: | 345 nm |
| Emission scan: | 440 nm |

**3.1.2 Sorbed to Cotton**

| | |
|---|---|
| Sensitivity: | high |
| Band width: | 3 nm |
| Synchronous scan: | $\Delta\lambda$ = 60 nm, vary emission wavelength between 350 nm & 550 nm |
| Excitation scan: | Emission wavelength = 440 nm, vary excitation wavelength between 300 nm & 430 nm |
| Emission scan: | Excitation wavelength = 380 nm, vary emission wavelength between 390 nm & 550 nm |

The presence of optical brighteners is indicated by peaks at the following wavelengths:

| | |
|---|---|
| Synchronous scan: | 440 nm |
| Excitation scan: | 380 nm |
| Emission scan: | 440 nm |

**3.1.3 Sorbed to Polyethersulfone**

| | |
|---|---|
| Sensitivity: | high |
| Band width: | 1.5 nm |
| Synchronous scan: | $\Delta\lambda$ = 65 nm, vary emission wavelength between 375 nm & 575 nm |
| Excitation scan: | Emission wavelength = 435 nm, vary excitation wavelength between 300 nm & 430 nm |
| Emission scan: | Excitation wavelength = 370 nm, vary emission wavelength between 380 nm & 525 nm |

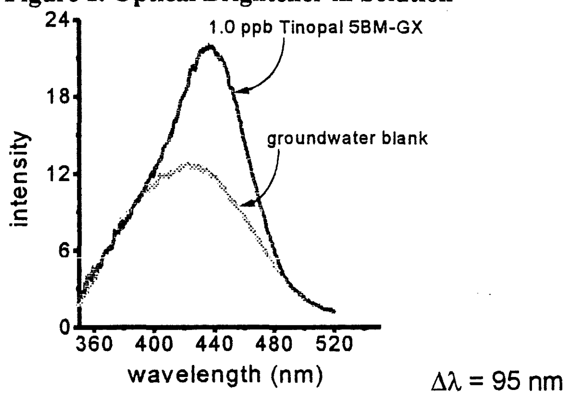
The presence of optical brighteners is indicated by peaks at the following wavelengths:

| | |
|---|---|
| Synchronous scan: | 435 nm |
| Excitation scan: | 370 nm |
| Emission scan: | 435 nm |

### 3.2 Detection in Direct Solution

Optical brighteners can be detected in solution. However, naturally occurring organic compounds present even in pristine groundwaters fluoresce at similar wavelengths causing interference at low optical brightener concentrations. Figure 1 contains synchronous scans of a pristine groundwater and of a 1.0 ppb solution of an optical brightener in groundwater. The interference problem is further compounded by the variability of natural groundwater fluorescence.

**Figure 1. Optical Brightener in Solution**

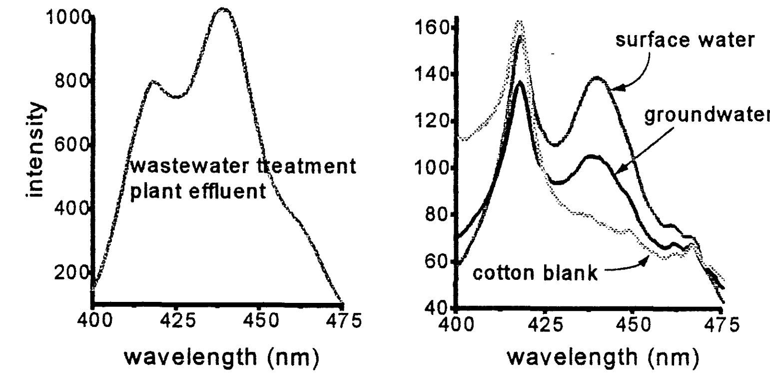



### 3.3 Detection on Cotton

Cotton immersed in water streams containing optical brighteners obtain peaks at wavelengths characteristic of optical brighteners and laundry detergents. Figure 2 contains some scans of samples considered positive for optical brighteners. The samples were exposed to various water environments. All of the spectra in figure 2 are synchronous scans ($\Delta\lambda$ = 60 nm) of cotton samples. Note that the graph on the left side of figure 2 (cotton after exposure to the effluent stream of a waste water treatment plant) has a much larger y axis, indicating a greater degree of brightening.



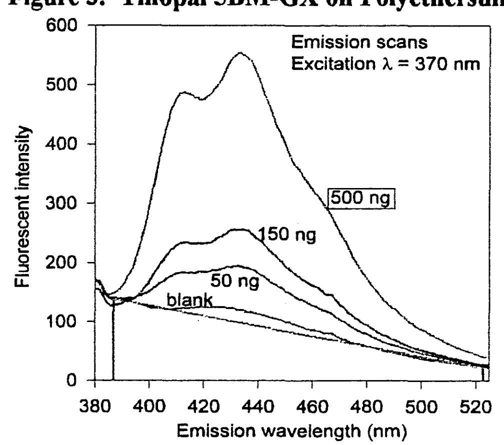
**Figure 2. Example Fluorescence Spectra of Cotton Samples Positive for Optical Brighteners**




### 3.4 Detection on Polyethersulfone

Optical brighteners accumulate on polyethersulfone filter membrane material. Figure 3 contains fluorescent spectra of filter media with various masses of optical brightener applied. Optical brighteners were applied to the filter medium using a syringe connected to a syringe tip filter. Optical brighteners produce peaks at characteristic wavelengths in the fluorescent spectrum of polyethersulfone. The area beneath the peaks increases with increasing sorbed mass of optical brighteners.

**Figure 3. Tinopal 5BM-GX on Polyethersulfone Filter Medium.**



### 3.5 Field Sampling Program Results Summary

Within field sample batches 1 through 38, cotton based immersion detectors appear to have functioned better than other detection methodologies. This section is a summary of the results of batches 3 through 38 inclusive. Batches 1 and 2 are not contained in this summary because detection parameters had not been optimized at the time of analysis. Cotton samples from batches 3 through 38 were analyzed in accordance with the settings described in section 3.1.2, with the exception of some samples being scanned with fluorometer band widths set at 5 nm rather than 3 nm. Table 1 contains a summary of sample submissions organized by batch number.

Each sample was analyzed at one or more locations on the surface of the cotton pad. This was achieved by repeatedly analyzing the cotton pad, and moving it around in the sample holder between scans. This methodology was followed in an attempt to address heterogeneity with respect to brightening across the surface of the pad.

Following fluorometric analysis a hard copy output was generated. Hard copy outputs were used to visually asses the sample fluorescence spectrum for the presence of characteristic peaks. If no peak above background at 440 nm in the synchronous scan was discernible the sample scan was designated N (negative). The observation of a peak at 440 nm caused the sample to be designated P (positive). In cases where the presence or absence of a peak could not easily be established a designation of I (indeterminable) was applied.

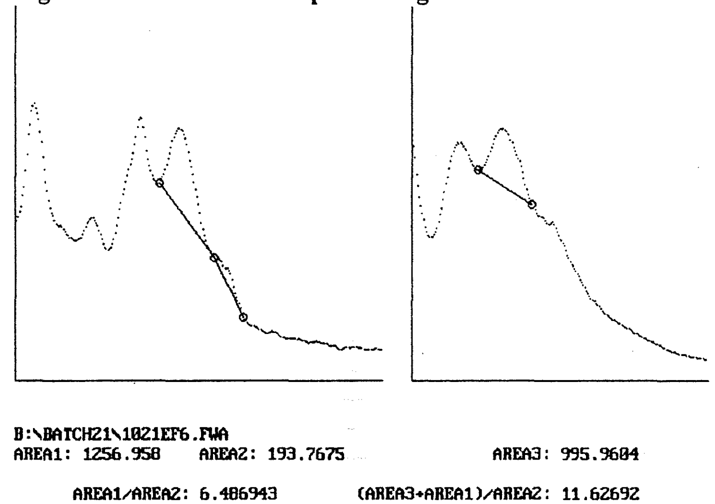
Fluorescence spectra were processed with a computer algorithm to calculate the ratio between peaks characteristic of optical brighteners to a set of peaks present in both blanks and positive samples. The term "optical brightener index" (OBI) is used to describe the ratio of specific optical brightener characteristic peak areas to specific background peak area. Figure 4 illustrates how the peak areas and OBI are calculated with an example. The OBI serves to quantify the size of the optical brightener peak and normalizes the optical brightener peak to the magnitude of the background peaks. Relatively larger characteristic optical brightener peaks produce larger values of OBI. Background portions of exposed sample scans vary over a wide range as a result of cotton surface contamination with bacterial deposits and solid particles.

The optical brightener index was calibrated to the visual observations of peak presence. The value of OBI which corresponded best to apparent visual cutoff between positive and indeterminable was 3.2. Table 2 is a summary of field sample analyses including visual classification and OBI for all scans.

Individual scan OBIs were then averaged to produce an overall sample OBI. Figure 5 combines OBI information (y axis, log scale) with exposure time information. Exposure time is defined as the length of time cotton immersion sample were in place in the field. The horizontal line at OBI = 3.2 represents the cutoff between positive and negative ' ·d on OBI.

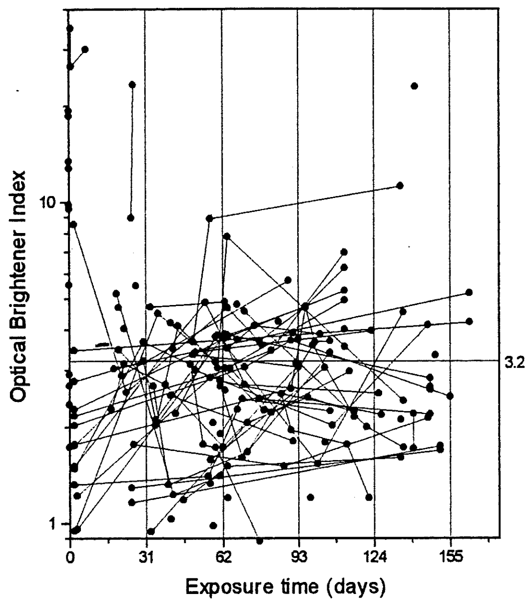


**Figure 4. Calculation of Optical Brightener Index**




Notes: Left pane = synchronous scan
Right pane = emission scan
Areas are numerically integrated between sloping straight line and signal
Area 1 = characteristic optical brightener peak in synchronous scan
Area 2 = background peaks
Area 3 = characteristic optical brightener peak in emission scan
Optical brightener index = (Area1 + Area3) / Area2

**Figure 5. Optical Brightener Index vs Exposure time**




Notes: Dots = individual samples
Lines connect samples from the same location



**Table 1. Summary of Field Sample Batches**

| Batch | submittal date | cotton samples | scans |
|---|---|---|---|
| 1 | 3/14/94 | 10 | 12 |
| 2 | 3/24/94 | 5 | 9 |
| 3 | 4/8/94 | 8 | 14 |
| 4 | 4/22/94 | 7 | 13 |
| 5 | 4/29/94 | 6 | 19 |
| 6 | 5/6/94 | 6 | 9 |
| 7 | 5/20/94 | 2 | 10 |
| 8 | 5/26/94 | 4 | 9 |
| 9 | 6/3/94 | 4 | 7 |
| 10 | 6/10/94 | 4 | 8 |
| 11 | 7/22/94 | 9 | 10 |
| 12 | 7/29/94 | 1 | 1 |
| 13 | 8/4/94 | 13 | 41 |
| 14 | 8/12/94 | 6 | 28 |
| 15 | 8/25/94 | 17 | 21 |
| 16 | 9/29/94 | 6 | 13 |
| 17 | 10/14/94 | 7 | 35 |
| 18 | 11/18/94 | 2 | 9 |
| 19 | 12/2/94 | 3 | 13 |
| 20 | 12/16/94 | 6 | 24 |
| 21 | 12/22/94 | 6 | 31 |
| 22 | 12/30/94 | 1 | 0 |
| 23 | 2/17/95 | 0 | 0 |
| 24 | 1/5/95 | 9 | 53 |
| 25 | 1/20/95 | 8 | 37 |
| 26 | 1/26/95 | 4 | 17 |
| 27 | 2/3/95 | 2 | 8 |
| 28 | 2/10/95 | 3 | 10 |
| 29 | 2/17/95 | 11 | 50 |
| 30 | 2/24/95 | 11 | 30 |
| 31 | 3/17/95 | 5 | 20 |
| 32 | 4/14/95 | 2 | 9 |
| 33 | 4/21/95 | 11 | 26 |
| 34 | 5/19/95 | 7 | 26 |
| 35 | 5/19/95 | 9 | 22 |
| 36 | 5/24/95 | 4 | 17 |
| 37 | 5/26/95 | 2 | 6 |
| 38 | 6/2/95 | 5 | 20 |
| **sum** | | **226** | **687** |

**Table 2. Summary of Field Data Scan Results**

| Filename | AREA1 | AREA2 | AREA3 | visual | OB Index |
|---|---|---|---|---|---|
| B:\BATCH3\1006AC.FWA | 64.24152 | 37.11459 | 57.88287 | I | 3.29 |
| B:\BATCH3\1006AC2.FWA | 25.09497 | 24.6507 | 25.58829 | N | 2.06 |
| B:\BATCH3\1006BC.FWA | 144.2389 | 98.23547 | 162.7982 | N | 3.13 |
| B:\BATCH3\1006BC2.FWA | 106.8265 | 52.49213 | 93.38477 | I | 3.81 |
| B:\BATCH3\3018AB.FWA | 8.723083 | 15.98326 | 9.872253 | N | 1.16 |
| B:\BATCH3\3019AB.FWA | 10.86612 | 14.25823 | 7.496124 | N | 1.29 |
| B:\BATCH3\3020AB.FWA | 718.2559 | 129.9148 | 556.354 | P | 9.81 |
| B:\BATCH3\3020AB3.FWA | 743.4932 | 159.7336 | 542.3359 | P | 8.05 |
| B:\BATCH3\1024AB.FWA | 219.0557 | 111.2532 | 214.2378 | I | 3.89 |
| B:\BATCH3\1024AB2.FWA | 380.9238 | 135.2125 | 360.0229 | P | 5.48 |
| B:\BATCH3\1031AC3.FWA | 147.0991 | 152.9989 | 162.6753 | N | 2.02 |
| B:\BATCH3\1031AC2.FWA | 143.3027 | 145.7317 | 157.9619 | N | 2.07 |
| B:\BATCH3\1031AC.FWA | 186.0369 | 153.4886 | 227.0447 | N | 2.69 |
| B:\BATCH3\BLNK0414.FWA | 100.1189 | 140.5249 | 149.1606 | N | 1.77 |
| B:\BATCH4\TTDC0426.FWA | 263.2715 | 184.1289 | 315.5015 | N | 3.14 |
| B:\BATCH4\0000BB.FWA | 271.7969 | 187.9686 | 311.6333 | N | 3.10 |
| B:\BATCH4\1002CD.FWA | 40.80841 | 73.98132 | 32.90808 | N | 1.00 |
| B:\BATCH4\1002CD1.FWA | 206.0713 | 462.3518 | 255.1841 | N | 1.00 |
| B:\BATCH4\1002CD2.FWA | 79.66089 | 191.4415 | 84.38208 | N | 0.86 |
| B:\BATCH4\1028BC1.FWA | 449.3486 | 326.0581 | 426.9009 | N | 2.69 |
| B:\BATCH4\1028BC2.FWA | 205.8782 | 152.1713 | 210.8889 | N | 2.74 |
| B:\BATCH4\1028BC3.FWA | 254.4951 | 183.8978 | 252.696 | N | 2.76 |
| B:\BATCH4\1028BC4.FWA | 1145.371 | 815.8184 | 1217.002 | N | 2.90 |
| B:\BATCH4\1031EF.FWA | 436.2773 | 551.2271 | 504.5654 | N | 1.71 |
| B:\BATCH4\1031EF1.FWA | 70.99902 | 76.60089 | 66.47937 | N | 1.79 |
| B:\BATCH4\1002BD.FWA | 337.7043 | 151.4861 | 344.5383 | P | 4.50 |
| B:\BATCH4\1028AC.FWA | 97.32056 | 99.06781 | 110.7031 | N | 2.10 |
| B:\BATCH5\1006BD1.FWA | 480.0059 | 788.0254 | 589.9238 | N | 1.36 |
| B:\BATCH5\1006BD.FWA | 73.46521 | 119.6225 | 79.60657 | N | 1.28 |
| B:\BATCH5\1007BC.FWA | 197.8145 | 750.98 | 505.833 | N | 0.94 |
| B:\BATCH5\1031AE.FWA | 693.0088 | 624.3047 | 866.0869 | N | 2.50 |
| B:\BATCH5\1031AE1.FWA | 462.5737 | 344.8176 | 516.5142 | I | 2.84 |
| B:\BATCH5\1031AE2.FWA | 74.8468 | 53.55316 | 74.20044 | I | 2.78 |
| B:\BATCH5\1031CE.FWA | 1511.336 | 958.0605 | 1578.91 | I | 3.23 |
| B:\BATCH5\1031CE1.FWA | 217.6233 | 143.6698 | 219.1929 | I | 3.04 |
| B:\BATCH5\1034BD1.FWA | 336.5103 | 442.9546 | 333.1626 | N | 1.51 |
| B:\BATCH5\1034BD.FWA | 52.02954 | 65.10715 | 45.73596 | N | 1.50 |
| B:\BATCH5\1035AB.FWA | 647.6719 | 793.1885 | 1032.227 | N | 2.12 |
| B:\BATCH5\1035AB1.FWA | 107.3062 | 125.1882 | 132.1741 | N | 1.91 |
| B:\BATCH6\SPONG.FWA | 1611.233 | 436.834 | 1510.592 | P | 7.15 |
| B:\BATCH6\1008BC.FWA | 118.1776 | 112.072 | 112.8855 | N | 2.06 |
| B:\BATCH6\1013BC.FWA | 5.399803 | 8.498367 | 6.620964 | N | 1.41 |
| B:\BATCH6\1013BC1.FWA | 42.24719 | 59.33759 | 36.28748 | N | 1.32 |
| B:\BATCH6\1013BC2.FWA | 283.8291 | 462.7769 | 294.584 | N | 1.25 |
| B:\BATCH6\1014BC.FWA | 221.3604 | 120.6746 | 201.3469 | I | 3.50 |
| B:\BATCH6\1021AB.FWA | 158.1169 | 85.8501 | 156.6774 | P | 3.67 |



| | | | | | |
|---|---|---|---|---|---|
| B:\BATCH6\1033AB.FWA | 49.19861 | 81.427 | 47.02869 | N | 1.18 |
| B:\BATCH6\1036AB.FWA | 76.67432 | 60.70697 | 60.51697 | N | 2.26 |
| B:\BATCH7\1039AB.FWA | 1055.566 | 224.8362 | 862.5029 | P | 8.53 |
| B:\BATCH7\4045AB.FWA | 4017.805 | 1374.067 | 3604.053 | P | 5.55 |
| B:\BATCH7\ALEY1.FWA | 326.4297 | 136.1217 | 252.4924 | P | 4.25 |
| B:\BATCH8\MPCACOTT.FWA | 199.0972 | 184.3373 | 247.6753 | N | 2.42 |
| B:\BATCH8\JOHNBLNK.FWA | 174.0908 | 150.2568 | 265.3989 | N | 2.92 |
| B:\BATCH8\1037BC1.FWA | 67.79919 | 75.46527 | 62.37646 | N | 1.72 |
| B:\BATCH8\1037BC2.FWA | 465.6289 | 493.7747 | 507.2588 | N | 1.97 |
| B:\BATCH8\1037BC3.FWA | 474.3105 | 644.4907 | 554.5518 | N | 1.60 |
| B:\BATCH8\1038AB1.FWA | 450.8516 | 440.0784 | 499.1279 | N | 2.16 |
| B:\BATCH8\4040AB.FWA | 1404.605 | 990.042 | 1653.66 | I | 3.09 |
| B:\BATCH8\4040AB1.FWA | 218.814 | 154.632 | 241.167 | N | 2.97 |
| B:\BATCH9\1003BD.FWA | 8.895752 | 16.50452 | 6.336899 | N | 0.92 |
| B:\BATCH9\1003BD1.FWA | 46.24878 | 110.0399 | 46.21313 | N | 0.84 |
| B:\BATCH9\1003CD1.FWA | 458.4355 | 506.5356 | 481.3408 | N | 1.86 |
| B:\BATCH9\1003CD2.FWA | 191.3247 | 261.2933 | 183.4546 | N | 1.43 |
| B:\BATCH9\1003CD3.FWA | 126.9634 | 229.9553 | 134.9956 | N | 1.14 |
| B:\BATCH9\1016AC.FWA | 70.72546 | 147.1224 | 73.0802 | N | 0.98 |
| B:\BATCH9\1026AB.FWA | 499.248 | 447.2668 | 591.9883 | N | 2.44 |
| B:\BATCH10\MILKSOCK.FWA | 1416.854 | 79.79077 | 1404.192 | P | 35.36 |
| B:\BATCH10\1047AB.FWA | 9.773438 | 26.30659 | 15.72412 | N | 0.97 |
| B:\BATCH10\1047AB1.FWA | 82.3208 | 197.9204 | 106.2234 | N | 0.95 |
| B:\BATCH10\1048AB1.FWA | 271.9854 | 515.8706 | 345.5283 | N | 1.20 |
| B:\BATCH10\1048AB.FWA | 47.77185 | 80.60101 | 52.52039 | N | 1.24 |
| B:\BATCH10\1049AB.FWA | -294.557 | 329.7144 | 64.25977 | N | -0.70 |
| B:\BATCH10\1050AB1.FWA | 201.7104 | 268.0105 | 225.6519 | N | 1.59 |
| B:\BATCH10\1050AB2.FWA | 54.87878 | 106.1146 | 55.29871 | N | 1.04 |
| B:\BATCH11\3044BC.FWA | 774.2681 | 40.31354 | 631.292 | P | 34.87 |
| B:\BATCH11\3044BD.FWA | 1858.23 | 129.3092 | 1571.151 | P | 26.52 |
| B:\BATCH11\BLNK0729.FWA | 241.5068 | 205.462 | 277.2964 | N | 2.53 |
| B:\BATCH11\1030AC1.FWA | 180.3872 | 208.6448 | 178.7603 | N | 1.72 |
| B:\BATCH11\1030AC2.FWA | 271.1553 | 557.7678 | 307.2568 | N | 1.04 |
| B:\BATCH11\1030AC3.FWA | 259.0322 | 664.8794 | 446.3418 | N | 1.06 |
| B:\BATCH11\1030AC4.FWA | 123.1609 | 243.3606 | 154.0664 | N | 1.14 |
| B:\BATCH11\1030AC5.FWA | 58.4939 | 126.4457 | 57.0343 | N | 0.91 |
| B:\BATCH11\1030AC6.FWA | 188.9419 | 331.0703 | 158.375 | N | 1.05 |
| B:\BATCH11\1030AC7.FWA | 417.6528 | 503.5398 | 331.5791 | N | 1.49 |
| B:\BATCH12\3044BE.FWA | 1516.072 | 93.00397 | 1274.344 | P | 30.00 |
| B:\BATCH13\TB0815.FWA | 367.6094 | 925.9736 | 960.2324 | N | 1.43 |
| B:\BATCH13\TB08152.FWA | 76.60498 | 137.5906 | 123.439 | N | 1.45 |
| B:\BATCH13\1002EF.FWA | 967.9492 | 971.4199 | 1319.043 | N | 2.35 |
| B:\BATCH13\1002EF2.FWA | 460.6572 | 252.3622 | 456.9854 | P | 3.64 |
| B:\BATCH13\1002EF3.FWA | 135.7734 | 296.7314 | 260.8442 | N | 1.34 |
| B:\BATCH13\1002EF4.FWA | 518.3091 | 197.1619 | 437.0554 | P | 4.85 |
| B:\BATCH13\1002EF5.FWA | 331.6189 | 167.8315 | 281.564 | P | 3.65 |
| B:\BATCH13\1003DE.FWA | 130.144 | 210.1967 | 125.9651 | N | 1.22 |
| B:\BATCH13\1003DE2.FWA | 126.0403 | 225.7113 | 113.3755 | N | 1.06 |
| B:\BATCH13\1003DE3.FWA | 318.4844 | 255.9849 | 259.0122 | N | 2.26 |

| | | | | | |
|---|---|---|---|---|---|
| B:\BATCH13\1003DE4.FWA | 728.4092 | 670.3394 | 622.0527 | N | 2.01 |
| B:\BATCH13\1003DE5.FWA | 509.9565 | 485.8823 | 484.4985 | N | 2.05 |
| B:\BATCH13\1007CD.FWA | 909.7676 | 755.9858 | 956.8418 | N | 2.47 |
| B:\BATCH13\1028DE.FWA | 316.7207 | 440.3096 | 357.5752 | N | 1.53 |
| B:\BATCH13\1029AB.FWA | 339.7266 | 396.0837 | 299.9365 | N | 1.61 |
| B:\BATCH13\1029AB2.FWA | 308.8716 | 302.6123 | 285.0688 | N | 1.96 |
| B:\BATCH13\1029AB3.FWA | 537.2949 | 708.7002 | 591.9834 | N | 1.59 |
| B:\BATCH13\1035CD.FWA | 815.9023 | 506.251 | 841.8867 | I | 3.27 |
| B:\BATCH13\1035CD2.FWA | 644.9717 | 500.7473 | 788.9248 | I | 2.86 |
| B:\BATCH13\1035CD3.FWA | 1432.731 | 554.0195 | 1297.403 | P | 4.93 |
| B:\BATCH13\1035CD4.FWA | 2804.291 | 1268.941 | 1224.209 | I | 3.17 |
| B:\BATCH13\1035CD5.FWA | 445.5337 | 193.7811 | 394.9497 | P | 4.34 |
| B:\BATCH13\1037AD.FWA | 105.1201 | 73.04382 | 85.203 | N | 2.61 |
| B:\BATCH13\1037AD2.FWA | 723.6582 | 491.7749 | 723.3809 | I | 2.94 |
| B:\BATCH13\1037AD3.FWA | 289.3442 | 280.9063 | 367.252 | N | 2.34 |
| B:\BATCH13\1039AC.FWA | 1011.718 | 355.5291 | 880.7686 | P | 5.32 |
| B:\BATCH13\1039AC2.FWA | 916.1895 | 439.6201 | 814.1641 | P | 3.94 |
| B:\BATCH13\1039AC3.FWA | 311.6453 | 265.7415 | 311.5029 | N | 2.34 |
| B:\BATCH13\1039AC4.FWA | 216.2676 | 132.4976 | 208.7546 | I | 3.21 |
| B:\BATCH13\1048AC.FWA | 79.90515 | 108.5038 | 64.88672 | N | 1.33 |
| B:\BATCH13\1048AC2.FWA | 1761.586 | 774.96 | 1598.557 | P | 4.34 |
| B:\BATCH13\1048AC3.FWA | 271.0896 | 118.2318 | 218.9585 | P | 4.14 |
| B:\BATCH13\1048AC4.FWA | 216.2673 | 262.84 | 191.103 | N | 1.55 |
| B:\BATCH13\1049AC.FWA | 186.0962 | 301.7854 | 194.6343 | N | 1.26 |
| B:\BATCH13\1049AC2.FWA | 600.8965 | 690.9658 | 714.4199 | N | 1.90 |
| B:\BATCH13\1050AC.FWA | 295.4272 | 487.7378 | 365.3701 | N | 1.35 |
| B:\BATCH13\1050AC2.FWA | 212.9424 | 339.6689 | 217.4434 | N | 1.27 |
| B:\BATCH13\1050AC3.FWA | 472.7607 | 632.1147 | 544.3105 | N | 1.61 |
| B:\BATCH13\1050AC5.FWA | 367.2935 | 530.5181 | 353.8384 | N | 1.36 |
| B:\BATCH13\1052AB2.FWA | 180.3582 | 302.5115 | 277.9551 | I | 1.52 |
| B:\BATCH13\1052AB.FWA | 3184.432 | 980.917 | 2005.076 | I | 5.29 |
| B:\BATCH14\JJBLNK.FWA | 797.8926 | 426.0479 | 966.3193 | N | 4.14 |
| B:\BATCH14\TB0824.FWA | 186.0742 | 206.3586 | 267.0918 | N | 2.20 |
| B:\BATCH14\TB08242.FWA | 1606.324 | 1339.327 | 820.125 | I | 1.81 |
| B:\BATCH14\1047AC.FWA | 686.8467 | 532.7139 | 700.2266 | N | 2.60 |
| B:\BATCH14\1047AC2.FWA | 900.0186 | 377.823 | 775.4146 | P | 4.43 |
| B:\BATCH14\1047AC3.FWA | 1014.842 | 623.019 | 1018.235 | N | 3.26 |
| B:\BATCH14\1047AC4.FWA | 1729.332 | 620.6431 | 1513.142 | P | 5.22 |
| B:\BATCH14\4041AB.FWA | 933.7383 | 314.9666 | 795.2241 | P | 5.49 |
| B:\BATCH14\4041AB2.FWA | 134.413 | 49.07159 | 109.8615 | P | 4.98 |
| B:\BATCH14\4041AB3.FWA | 93.66571 | 41.61386 | 79.33203 | P | 4.16 |
| B:\BATCH14\4041AB4.FWA | 644.4824 | 269.3442 | 564.8066 | P | 4.49 |
| B:\BATCH14\4045AB5.FWA | 88.82739 | 126.3483 | 81.2926 | N | 1.35 |
| B:\BATCH14\4041AB6.FWA | 903.0601 | 366.3999 | 818.561 | P | 4.70 |
| B:\BATCH14\4041AB7.FWA | 138.0423 | 55.74896 | 114.5302 | P | 4.53 |
| B:\BATCH14\1033CD.FWA | 88.03711 | 670.1719 | 331.96 | N | 0.63 |
| B:\BATCH14\1033CD2.FWA | 246.7874 | 181.0231 | 241.8525 | N | 2.70 |
| B:\BATCH14\1033CD3.FWA | 61.26355 | 80.92975 | 64.52417 | N | 1.55 |
| B:\BATCH14\1033CD4.FWA | 66.94922 | 132.6348 | 86.40186 | N | 1.16 |



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|---|---|---|---|---|---|
| B:\BATCH14\1021CD.FWA | 979.1033 | 123.5797 | 783.4587 | P | 14.26 |
| B:\BATCH14\1021CD3.FWA | 187.7305 | 102.3852 | 159.4624 | P | 3.39 |
| B:\BATCH14\1021CD2.FWA | 707.6599 | 140.0688 | 553.7207 | P | 9.01 |
| B:\BATCH14\1009BC.FWA | 300.8418 | 67.13959 | 255.6953 | P | 8.29 |
| B:\BATCH14\1009BC2.FWA | 3909.287 | 183.176 | 2958.235 | P | 37.49 |
| B:\BATCH14\1051AB.FWA | 202.334 | 114.7208 | 209.2009 | N | 3.59 |
| B:\BATCH14\1051AB2.FWA | 118.5297 | 109.5722 | 134.7584 | N | 2.31 |
| B:\BATCH14\1051AB3.FWA | 181.5396 | 158.316 | 203.6602 | N | 2.43 |
| B:\BATCH14\3056AB.FWA | 104.7395 | 40.53046 | 91.50958 | P | 4.84 |
| B:\BATCH14\3056AB2.FWA | 732.6226 | 249.349 | 644.231 | P | 5.52 |
| B:\BATCH15\3057AB.FWA | 62.35242 | 80.08423 | 61.9425 | N | 1.55 |
| B:\BATCH15\3057AB2.FWA | 44.81799 | 53.68536 | 46.85681 | N | 1.71 |
| B:\BATCH15\3057AB3.FWA | 60.1554 | 57.33603 | 55.88989 | N | 2.02 |
| B:\BATCH15\1039CD.FWA | 263.3616 | 127.8607 | 334.7664 | P | 4.68 |
| B:\BATCH15\1039CD2.FWA | 50.60059 | 73.08887 | 107.1173 | N | 2.16 |
| B:\BATCH15\1039CD3.FWA | 64.82074 | 74.1821 | 63.51971 | N | 1.73 |
| B:\BATCH15\1039CD4.FWA | 382.731 | 488.0881 | 432.5747 | N | 1.67 |
| B:\BATCH15\JS0831.FWA | 255.1338 | 322.7153 | 337.0308 | N | 1.83 |
| B:\BATCH15\3065A1.FWA | 644.8765 | 222.7373 | 586.0835 | P | 5.53 |
| B:\BATCH15\3065A2.FWA | 1663.68 | 315.0142 | 1332.524 | P | 9.51 |
| B:\BATCH15\3065A3.FWA | 1289.31 | 239.6094 | 1060.871 | P | 9.81 |
| B:\BATCH15\3065A4.FWA | 2299.715 | 315.7795 | 1938.158 | P | 13.42 |
| B:\BATCH15\3065A5.FWA | 2435.122 | 343.3081 | 1950.018 | P | 12.77 |
| B:\BATCH15\3065A6.FWA | 3197.238 | 295.3811 | 2510.032 | P | 19.32 |
| B:\BATCH15\3065A7.FWA | 1763.18 | 171.2766 | 1425.106 | P | 18.61 |
| B:\BATCH15\3020CD.FWA | 1028.228 | 81.82697 | 873.1443 | P | 23.24 |
| B:\BATCH15\3066A1.FWA | 301.4927 | 215.7544 | 325.4839 | N | 2.91 |
| B:\BATCH15\3066A2.FWA | 209.4929 | 182.1912 | 216.4551 | N | 2.34 |
| B:\BATCH15\3066A3.FWA | 195.1926 | 146.0656 | 198.4434 | N | 2.69 |
| B:\BATCH15\3066A4.FWA | 264.4851 | 173.7831 | 241.283 | N | 2.91 |
| B:\BATCH15\3066A5.FWA | 113.8792 | 142.9283 | 133.7383 | N | 1.73 |
| B:\BATCH16\3064AB.FWA | 34.18597 | 44.04492 | 44.82056 | N | 1.79 |
| B:\BATCH16\3064AB2.FWA | 77.02094 | 44.06985 | 64.26385 | P | 3.21 |
| B:\BATCH16\3056AC.FWA | 9.193985 | 13.6254 | 10.02792 | N | 1.41 |
| B:\BATCH16\3056BC.FWA | 9.534546 | 25.0134 | 19.25833 | N | 1.15 |
| B:\BATCH16\3056BC2.FWA | 16.66803 | 26.96616 | 21.0029 | N | 1.40 |
| B:\BATCH16\3056BC3.FWA | 16.39813 | 37.87524 | 26.31006 | N | 1.13 |
| B:\BATCH16\3056BC4.FWA | 18.20575 | 39.40512 | 30.07269 | N | 1.23 |
| B:\BATCH16\5062AB.FWA | 502.7268 | 156.6088 | 394.719 | P | 5.73 |
| B:\BATCH16\5062AB2.FWA | 339.0586 | 141.2217 | 281.0498 | P | 4.39 |
| B:\BATCH16\5062AB3.FWA | 353.7444 | 132.5881 | 284.604 | P | 4.81 |
| B:\BATCH16\5062AB4.FWA | 143.9883 | 143.9989 | 131.3301 | N | 1.91 |
| B:\BATCH16\5063AB.FWA | 17.63248 | 36.68837 | 23.37335 | N | 1.12 |
| B:\BATCH16\5063AB2.FWA | 21.2196 | 54.27591 | 29.85931 | N | 0.94 |
| B:\BATCH17\1050CD.FWA | 73.38428 | 83.66492 | 76.53796 | N | 1.79 |
| B:\BATCH17\1050CD2.FWA | 81.30615 | 60.25909 | 69.33325 | N | 2.50 |
| B:\BATCH17\1050CD3.FWA | 63.87793 | 80.02319 | 62.599 | N | 1.58 |
| B:\BATCH17\1050CD4.FWA | 143.7122 | 123.4009 | 158.3145 | N | 2.45 |
| B:\BATCH17\1050CD5.FWA | 128.8215 | 117.3518 | 144.8745 | N | 2.33 |

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|---|---|---|---|---|---|
| B:\BATCH17\1050CD6.FWA | 227.979 | 155.1086 | 226.8237 | N | 2.93 |
| B:\BATCH17\1034EF.FWA | 142.8243 | 107.7346 | 137.105 | N | 2.60 |
| B:\BATCH17\1034EF2.FWA | 84.72131 | 84.47156 | 79.70105 | N | 1.95 |
| B:\BATCH17\1034EF3.FWA | 207.9348 | 145.0922 | 213.3982 | N | 2.90 |
| B:\BATCH17\1034EF4.FWA | 141.2838 | 80.54279 | 125.3735 | P | 3.31 |
| B:\BATCH17\1034EF5.FWA | 168.4314 | 111.7986 | 164.9089 | N | 2.98 |
| B:\BATCH17\1034EF6.FWA | 212.8618 | 141.9271 | 218.1953 | N | 3.04 |
| B:\BATCH17\1034EF7.FWA | 92.48462 | 81.52026 | 86.06787 | N | 2.19 |
| B:\BATCH17\1029BC.FWA | 154.8616 | 96.55566 | 133.6085 | I | 2.99 |
| B:\BATCH17\1029BC2.FWA | 537.6917 | 140.1143 | 459.884 | P | 7.12 |
| B:\BATCH17\1029BC3.FWA | 426.5745 | 157.5137 | 365.3672 | P | 5.03 |
| B:\BATCH17\1029BC4.FWA | 277.3115 | 107.9203 | 236.4531 | P | 4.76 |
| B:\BATCH17\1029BC5.FWA | 121.4038 | 73.26364 | 93.77075 | I | 2.94 |
| B:\BATCH17\4041BC.FWA | 268.9521 | 112.8602 | 257.0684 | P | 4.66 |
| B:\BATCH17\4041BC2.FWA | 129.7878 | 143.3894 | 157.8884 | N | 2.01 |
| B:\BATCH17\4041BC3.FWA | 151.0276 | 157.4435 | 167.8149 | N | 2.03 |
| B:\BATCH17\4041BC4.FWA | 320.4805 | 122.5669 | 278.7625 | P | 4.89 |
| B:\BATCH17\4041BC5.FWA | 388.1167 | 118.0054 | 328.855 | P | 6.08 |
| B:\BATCH17\4041BC6.FWA | 325.709 | 168.3766 | 319.5376 | P | 3.83 |
| B:\BATCH17\4041BC7.FWA | 192.2473 | 67.45392 | 160.0858 | P | 5.22 |
| B:\BATCH17\4041BC8.FWA | 38.20212 | 34.63643 | 37.22012 | N | 2.18 |
| B:\BATCH17\4059AB.FWA | 9.707542 | 17.25636 | 3.325577 | N | 0.76 |
| B:\BATCH17\4059AB2.FWA | 24.82416 | 39.74539 | 15.78214 | N | 1.02 |
| B:\BATCH17\4059AB3.FWA | 50.78757 | 51.0274 | 42.28802 | N | 1.82 |
| B:\BATCH17\1006EF.FWA | 35.86029 | 42.42981 | 25.23401 | N | 1.44 |
| B:\BATCH17\1006EF2.FWA | 14.57501 | 18.50989 | 12.88098 | N | 1.48 |
| B:\BATCH17\1006EF3.FWA | 55.96606 | 54.38242 | 51.23694 | N | 1.97 |
| B:\BATCH17\1006EF4.FWA | 45.56226 | 45.16711 | 34.96259 | N | 1.78 |
| B:\BATCH17\1007DE.FWA | 142.3185 | 105.965 | 121.4249 | N | 2.49 |
| B:\BATCH17\1007DE2.FWA | 79.90369 | 106.6923 | 93.20044 | N | 1.62 |
| B:\BATCH18\1037DE.FWA | 176.879 | 84.81915 | 161.0226 | P | 3.98 |
| B:\BATCH18\1037DE2.FWA | 152.5953 | 69.56491 | 123.1317 | P | 3.96 |
| B:\BATCH18\1037DE3.FWA | 210.1531 | 133.6107 | 209.134 | I | 3.14 |
| B:\BATCH18\1049CD.FWA | 125.6835 | 110.9826 | 109.9204 | N | 2.12 |
| B:\BATCH18\1049CD2.FWA | 127.0492 | 94.68311 | 124.7419 | N | 2.66 |
| B:\BATCH18\1049CD3.FWA | 268.6943 | 124.1603 | 235.2358 | P | 4.06 |
| B:\BATCH18\1049CD4.FWA | 185.4039 | 98.89594 | 158.8396 | P | 3.48 |
| B:\BATCH18\1049CD5.FWA | 160.1824 | 65.59671 | 134.2068 | P | 4.49 |
| B:\BATCH18\1049CD6.FWA | 91.81982 | 120.2442 | 97.37769 | N | 1.57 |
| B:\BATCH19\1030DE.FWA | 8.523094 | 9.180069 | 7.863464 | N | 1.79 |
| B:\BATCH19\1030DE3.FWA | 23.97668 | 25.69525 | 19.9595 | N | 1.71 |
| B:\BATCH19\1030DE2.FWA | 49.12646 | 48.94968 | 37.62433 | N | 1.77 |
| B:\BATCH19\1030DE4.FWA | 14.80971 | 15.07815 | 11.92805 | N | 1.77 |
| B:\BATCH19\1048CD.FWA | 156.5055 | 51.99734 | 123.5352 | P | 5.39 |
| B:\BATCH19\1048CD2.FWA | 157.5888 | 51.61868 | 116.376 | P | 5.31 |
| B:\BATCH19\1048CD4.FWA | 106.505 | 52.96689 | 83.38232 | P | 3.59 |
| B:\BATCH19\1048CD5.FWA | 172.8965 | 58.7876 | 135.3239 | P | 5.24 |
| B:\BATCH19\1048CD6.FWA | 211.4496 | 70.37219 | 157.6014 | P | 5.24 |
| B:\BATCH19\1038CD.FWA | 56.79861 | 32.68774 | 41.09613 | N | 2.[illegible] |



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|---|---|---|---|---|---|
| B:\BATCH19\1038CD2.FWA | 109.2648 | 64.41357 | 87.23181 | N | 3.05 |
| B:\BATCH19\1038CD3.FWA | 85.95483 | 50.7887 | 68.28601 | N | 3.04 |
| B:\BATCH19\1038CD5.FWA | 96.84875 | 65.79401 | 89.68311 | N | 2.84 |
| B:\BATCH20\1002FG2.FWA | 16.50377 | 10.34686 | 8.437424 | N | 2.41 |
| B:\BATCH20\1002FG.FWA | 11.97152 | 8.524246 | 7.071495 | N | 2.23 |
| B:\BATCH20\1002FG3.FWA | 16.9404 | 17.9317 | 10.19705 | N | 1.51 |
| B:\BATCH20\1002FG4.FWA | 31.83411 | 32.8725 | 31.34943 | N | 1.92 |
| B:\BATCH20\1002FG5.FWA | 32.99121 | 16.32745 | 22.93417 | P | 3.43 |
| B:\BATCH20\1002FG6.FWA | 35.49866 | 22.62854 | 31.49625 | I | 2.96 |
| B:\BATCH20\1028EF.FWA | 50.55707 | 22.87851 | 34.5524 | P | 3.72 |
| B:\BATCH20\1028EF2.FWA | 61.22913 | 20.74809 | 40.48981 | P | 4.90 |
| B:\BATCH20\1028EF3.FWA | 75.72522 | 22.75337 | 50.21857 | P | 5.54 |
| B:\BATCH20\1028EF4.FWA | 59.5871 | 24.84042 | 39.14246 | P | 3.97 |
| B:\BATCH20\1036CD.FWA | 132.4381 | 47.25977 | 118.329 | P | 5.31 |
| B:\BATCH20\1036CD2.FWA | 126.0251 | 47.94751 | 103.6127 | P | 4.79 |
| B:\BATCH20\1036CD3.FWA | 73.01001 | 20.29234 | 55.65564 | P | 6.34 |
| B:\BATCH20\1036CD4.FWA | 94.81104 | 36.93085 | 80.52002 | P | 4.75 |
| B:\BATCH20\1039DE.FWA | 55.04907 | 17.23402 | 54.33408 | P | 6.35 |
| B:\BATCH20\1039DE4.FWA | 65.78296 | 16.91096 | 58.72562 | P | 7.36 |
| B:\BATCH20\1039DE2.FWA | 63.72531 | 20.2242 | 57.96924 | P | 6.02 |
| B:\BATCH20\1039DE3.FWA | 62.14038 | 22.32814 | 55.39984 | P | 5.26 |
| B:\BATCH20\1051BC.FWA | 67.65637 | 53.36124 | 79.28284 | N | 2.75 |
| B:\BATCH20\1051BC3.FWA | 17.83539 | 23.04868 | 19.2121 | N | 1.61 |
| B:\BATCH20\1052BC.FWA | 63.69275 | 30.58734 | 51.98547 | P | 3.78 |
| B:\BATCH20\1052BC2.FWA | 24.15945 | 12.34023 | 17.73672 | P | 3.40 |
| B:\BATCH20\1052BC3.FWA | 66.87909 | 33.49255 | 48.52252 | I | 3.45 |
| B:\BATCH20\1052BC4.FWA | 67.83356 | 22.02888 | 48.67148 | P | 5.29 |
| B:\BATCH21\1058AB.FWA | 119.604 | 133.5867 | 126.6548 | N | 1.84 |
| B:\BATCH21\1058AB2.FWA | 121.574 | 137.2052 | 124.3137 | N | 1.79 |
| B:\BATCH21\1058C.FWA | 179.4897 | 168.0151 | 189.6616 | N | 2.20 |
| B:\BATCH21\1058ABD.FWA | 82.7583 | 127.4763 | 108.0625 | N | 1.50 |
| B:\BATCH21\TB1221.FWA | 265.1992 | 201.3137 | 300.0537 | N | 2.81 |
| B:\BATCH21\TB1221B.FWA | 277.6665 | 210.5999 | 343.1572 | N | 2.95 |
| B:\BATCH21\TB1221C.FWA | 298.7788 | 214.6036 | 373.5244 | N | 3.13 |
| B:\BATCH21\TB1221D.FWA | 1982.49 | 492.6631 | 1840.785 | P | 7.76 |
| B:\BATCH21\TB1221E.FWA | 2755.894 | 606.7178 | 2475.506 | P | 8.62 |
| B:\BATCH21\TB1221F.FWA | 1787.519 | 446.748 | 1708.679 | P | 7.83 |
| B:\BATCH21\TB1221G.FWA | 818.6724 | 313.3545 | 835.2002 | P | 5.28 |
| B:\BATCH21\TB1221H.FWA | 309.7783 | 213.9391 | 370.3711 | N | 3.18 |
| B:\BATCH21\TB1221I.FWA | 251.3457 | 228.4747 | 326.2925 | N | 2.53 |
| B:\BATCH21\TB1221J.FWA | 382.8047 | 272.2986 | 478.1812 | N | 3.16 |
| B:\BATCH21\1021EF.FWA | 424.6133 | 171.9004 | 365.7129 | P | 4.60 |
| B:\BATCH21\1021EF2.FWA | 315.2429 | 193.0505 | 304.1272 | P | 3.21 |
| B:\BATCH21\1021EF3.FWA | 295.0845 | 154.1138 | 269.4321 | P | 3.66 |
| B:\BATCH21\1021EF4.FWA | 386.4634 | 164.2545 | 333.3481 | P | 4.38 |
| B:\BATCH21\1021EF5.FWA | 3485.063 | 328.1423 | 2803.983 | P | 19.17 |
| B:\BATCH21\1021EF6.FWA | 1256.958 | 193.7675 | 995.9604 | P | 11.63 |
| B:\BATCH21\1021EF7.FWA | 6708.594 | 533.3481 | 4999.297 | P | 21.95 |
| B:\BATCH21\1021EF8.FWA | 4411.658 | 377.5137 | 3521.851 | P | 21.02 |

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|---|---|---|---|---|---|
| B:\BATCH21\1033DE.FWA | 75.62598 | 113.5691 | 77.2832 | N | 1.35 |
| B:\BATCH21\1033DE2.FWA | 89.87085 | 124.5671 | 80.82715 | N | 1.37 |
| B:\BATCH21\1033DE3.FWA | 102.0137 | 83.98901 | 89.02234 | N | 2.27 |
| B:\BATCH21\1033DE4.FWA | 91.09351 | 128.5467 | 109.5681 | N | 1.56 |
| B:\BATCH21\1033DE5.FWA | 79.4043 | 111.3033 | 80.95361 | N | 1.44 |
| B:\BATCH21\1060AB.FWA | 62.21704 | 58.5636 | 51.85187 | N | 1.95 |
| B:\BATCH21\1060AB3.FWA | 82.96448 | 66.75546 | 82.40259 | N | 2.48 |
| B:\BATCH21\1060AB4.FWA | 54.54065 | 56.80301 | 46.2962 | N | 1.78 |
| B:\BATCH21\1060AB5.FWA | 160.4111 | 141.9913 | 154.9053 | N | 2.22 |
| B:\BATCH24\1026CD1.FWA | 79.24707 | 124.9088 | 87.34302 | N | 1.33 |
| B:\BATCH24\1026CD2.FWA | 132.3545 | 64.62659 | 100.1064 | I | 3.60 |
| B:\BATCH24\1026CD3.FWA | 56.23572 | 64.17154 | 41.6745 | N | 1.53 |
| B:\BATCH24\1026CD4.FWA | 270.2217 | 159.72 | 236.9888 | I | 3.18 |
| B:\BATCH24\1026CD5.FWA | 90.70215 | 144.468 | 99.2478 | N | 1.31 |
| B:\BATCH24\1035DE1.FWA | 212.0625 | 79.6933 | 174.598 | P | 4.85 |
| B:\BATCH24\1035DE2.FWA | 68.3681 | 52.14813 | 64.44586 | N | 2.55 |
| B:\BATCH24\1035DE3.FWA | 124.3816 | 152.8608 | 129.3882 | N | 1.66 |
| B:\BATCH24\1035DE4.FWA | 103.6409 | 93.88745 | 86.26782 | N | 2.02 |
| B:\BATCH24\1035DE5.FWA | 49.03357 | 38.5441 | 52.25519 | N | 2.63 |
| B:\BATCH24\1035DE6.FWA | 73.27966 | 67.08453 | 75.73328 | N | 2.22 |
| B:\BATCH24\1035DE7.FWA | 103.1978 | 151.2205 | 109.8105 | N | 1.41 |
| B:\BATCH24\1047CD1.FWA | 180.2241 | 124.8344 | 160.5432 | N | 2.73 |
| B:\BATCH24\1047CD2.FWA | 193.9626 | 138.3822 | 190.427 | I | 2.78 |
| B:\BATCH24\1047CD3.FWA | 242.4465 | 140.5441 | 214.707 | I | 3.25 |
| B:\BATCH24\1047CD4.FWA | 196.9086 | 111.9284 | 168.1565 | P | 3.26 |
| B:\BATCH24\1047CD5.FWA | 93.44189 | 63.02853 | 76.20868 | I | 2.69 |
| B:\BATCH24\1047CD6.FWA | 95.15302 | 75.0574 | 75.56616 | N | 2.27 |
| B:\BATCH24\1080AB1.FWA | 101.0232 | 166.9305 | 134.6143 | N | 1.41 |
| B:\BATCH24\1080AB2.FWA | 172.1719 | 132.798 | 185.7993 | N | 2.70 |
| B:\BATCH24\1080AB3.FWA | 373.377 | 131.5188 | 351.3174 | P | 5.51 |
| B:\BATCH24\1080AB4.FWA | 363.6057 | 150.4559 | 344.95 | P | 4.71 |
| B:\BATCH24\1080AB5.FWA | 360.2378 | 172.0803 | 356.229 | P | 4.16 |
| B:\BATCH24\1080AB7.FWA | 119.197 | 168.4637 | 155.9333 | N | 1.63 |
| B:\BATCH24\1069AB1.FWA | 136.7537 | 118.402 | 124.4619 | N | 2.21 |
| B:\BATCH24\1069AB2.FWA | 97.39258 | 122.3085 | 113.3215 | N | 1.72 |
| B:\BATCH24\1069AB3.FWA | 174.6063 | 82.68176 | 156.9861 | P | 4.01 |
| B:\BATCH24\1069AB4.FWA | 118.305 | 59.4696 | 95.98157 | P | 3.60 |
| B:\BATCH24\1069AB5.FWA | 179.5878 | 96.36432 | 154.9285 | P | 3.47 |
| B:\BATCH24\1081AB1.FWA | 152.3554 | 57.14285 | 123.4229 | P | 4.83 |
| B:\BATCH24\1081AB2.FWA | 542.3013 | 135.2593 | 444.7275 | P | 7.30 |
| B:\BATCH24\1081AB3.FWA | 305.2532 | 138.1849 | 272.5515 | P | 4.18 |
| B:\BATCH24\1081AB4.FWA | 248.8687 | 123.2756 | 228.3369 | P | 3.87 |
| B:\BATCH24\1081AB5.FWA | 189.4042 | 84.37543 | 152.2609 | P | 4.05 |
| B:\BATCH24\1081AB6.FWA | 45.9021 | 40.65302 | 35.08264 | N | 1.99 |
| B:\BATCH24\1081AB7.FWA | 255.3916 | 138.3022 | 206.2202 | P | 3.34 |
| B:\BATCH24\1081AB8.FWA | 224.3877 | 124.0712 | 188.5759 | P | 3.33 |
| B:\BATCH24\8053BC1.FWA | 46.05627 | 35.19148 | 35.28937 | N | 2.31 |
| B:\BATCH24\8053BC2.FWA | 70.59521 | 75.99762 | 62.34192 | N | 1.75 |
| B:\BATCH24\8053BC3.FWA | 44.57202 | 28.11105 | 32.98383 | N | 2.76 |



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|---|---|---|---|---|---|
| B:\BATCH24\8053BC4.FWA | 121.6565 | 119.7777 | 131.7104 | N | 2.12 |
| B:\BATCH24\8054BC1.FWA | 31.15112 | 29.41643 | 30.33081 | N | 2.09 |
| B:\BATCH24\8054BC2.FWA | 134.9487 | 139.293 | 115.783 | N | 1.80 |
| B:\BATCH24\8054BC3.FWA | 307.0959 | 133.7108 | 241.3799 | P | 4.10 |
| B:\BATCH24\8054BC4.FWA | 226.3076 | 122.4144 | 187.7449 | I | 3.38 |
| B:\BATCH24\8054BC5.FWA | 414.9617 | 136.826 | 340.5535 | P | 5.52 |
| B:\BATCH24\8054BC6.FWA | 189.3716 | 114.4398 | 173.312 | N | 3.17 |
| B:\BATCH24\8054BC7.FWA | 156.0015 | 93.68707 | 141.7802 | N | 3.18 |
| B:\BATCH24\8054BC8.FWA | 142.225 | 61.72009 | 100.6665 | P | 3.94 |
| B:\BATCH24\TB0112A.FWA | 568.9727 | 223.6689 | 590.458 | P | 5.18 |
| B:\BATCH24\TB0112B.FWA | 181.4458 | 189.8203 | 247.3147 | N | 2.26 |
| B:\BATCH24\TB0112C.FWA | 135.0295 | 184.6936 | 205.7258 | N | 1.84 |
| B:\BATCH24\TB0112D.FWA | 177.0059 | 206.3164 | 248.4131 | N | 2.06 |
| B:\BATCH25\TB0125A.FWA | 110.3154 | 176.3958 | 161.7437 | N | 1.54 |
| B:\BATCH25\TB0125B.FWA | 130.9849 | 197.5479 | 180.9146 | N | 1.58 |
| B:\BATCH25\TB0125C.FWA | 162.2815 | 201.7362 | 205.5469 | N | 1.82 |
| B:\BATCH25\TB0125D.FWA | 188.1079 | 201.4098 | 224.4438 | N | 2.05 |
| B:\BATCH25\TB0125E.FWA | 207.3823 | 196.002 | 232.8057 | N | 2.25 |
| B:\BATCH25\TB0125F.FWA | 145.8286 | 206.9568 | 203.8931 | N | 1.69 |
| B:\BATCH25\TB0125HA.FWA | 200.6724 | 199.2594 | 239.5903 | N | 2.21 |
| B:\BATCH25\TB0125HB.FWA | 338.5093 | 259.9243 | 384.3687 | N | 2.78 |
| B:\BATCH25\TB0125HC.FWA | 223.9272 | 234.5133 | 272.7002 | N | 2.12 |
| B:\BATCH25\TB0125HD.FWA | 236.6865 | 213.0736 | 265.4785 | N | 2.36 |
| B:\BATCH25\TB0125HE.FWA | 229.3687 | 195.8274 | 260.999 | N | 2.50 |
| B:\BATCH25\TB0125HF.FWA | 172.4082 | 210.9708 | 246.2544 | N | 1.98 |
| B:\BATCH25\3017BC1.FWA | 458.8281 | 185.428 | 413.5745 | P | 4.70 |
| B:\BATCH25\3017BC2.FWA | 384.5808 | 180.0421 | 332.179 | P | 3.98 |
| B:\BATCH25\3017BC3.FWA | 395.8911 | 180.6332 | 350.8406 | P | 4.13 |
| B:\BATCH25\3017BC4.FWA | 294.26 | 169.9207 | 254.4055 | P | 3.23 |
| B:\BATCH25\3017BC5.FWA | 245.2612 | 175.8438 | 237.3596 | N | 2.74 |
| B:\BATCH25\3017BC6.FWA | 298.6187 | 199.5382 | 266.6621 | I | 2.83 |
| B:\BATCH25\3017BC7.FWA | 290.7014 | 199.2211 | 287.4915 | N | 2.90 |
| B:\BATCH25\3018CD1.FWA | 66.86884 | 59.47272 | 65.88544 | N | 2.23 |
| B:\BATCH25\3018CD2.FWA | 21.21826 | 37.42288 | 25.25153 | N | 1.24 |
| B:\BATCH25\3019CD1.FWA | 58.53833 | 68.54395 | 54.77826 | N | 1.65 |
| B:\BATCH25\3019CD2.FWA | 101.314 | 96.81158 | 109.0054 | N | 2.17 |
| B:\BATCH25\3019CD3.FWA | 19.25055 | 32.63925 | 22.05078 | N | 1.27 |
| B:\BATCH25\3019CD4.FWA | 115.4801 | 133.5916 | 105.3733 | N | 1.65 |
| B:\BATCH25\4045CD1.FWA | 203.1707 | 92.21106 | 209.7672 | P | 4.48 |
| B:\BATCH25\4045CD2.FWA | 178.5164 | 101.9424 | 177.9808 | P | 3.50 |
| B:\BATCH25\4045CD3.FWA | 260.0996 | 152.0004 | 240.7876 | P | 3.30 |
| B:\BATCH25\4045CD4.FWA | 236.0808 | 104.9846 | 219.5143 | P | 4.34 |
| B:\BATCH25\4045CD5.FWA | 308.4309 | 110.7587 | 299.7256 | P | 5.49 |
| B:\BATCH25\4040DE1.FWA | 404.1824 | 134.1496 | 337.3015 | P | 5.53 |
| B:\BATCH25\4040DE2.FWA | 461.196 | 111.5459 | 364.259 | P | 7.40 |
| B:\BATCH25\4040DE3.FWA | 330.6196 | 143.8617 | 284.9702 | P | 4.28 |
| B:\BATCH25\4040DE4.FWA | 188.2064 | 92.28461 | 148.131 | P | 3.64 |
| B:\BATCH25\1006FG1.FWA | 166.3201 | 134.1534 | 163.4575 | N | 2.46 |
| B:\BATCH25\1006FG2.FWA | 340.6951 | 138.4786 | 296.5574 | P | 4.60 |

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|---|---|---|---|---|---|
| B:\BATCH25\1006FG3.FWA | 232.1716 | 119.6707 | 211.3804 | P | 3.71 |
| B:\BATCH26\1084AB1.FWA | 113.0208 | 104.3262 | 97.87988 | N | 2.02 |
| B:\BATCH26\1084AB2.FWA | 183.6135 | 172.0242 | 170.4436 | N | 2.06 |
| B:\BATCH26\1084AB3.FWA | 217.03 | 79.56378 | 146.1929 | P | 4.57 |
| B:\BATCH26\1084AB4.FWA | 260.473 | 107.4835 | 168.061 | P | 3.99 |
| B:\BATCH26\1084AB5.FWA | 282.9106 | 229.7134 | 300.29 | N | 2.54 |
| B:\BATCH26\3017BD1.FWA | 357.252 | 190.865 | 319.9595 | P | 3.55 |
| B:\BATCH26\3017BD2.FWA | 307.0237 | 136.0382 | 256.1882 | P | 4.14 |
| B:\BATCH26\3017BD3.FWA | 383.2432 | 194.386 | 332.396 | P | 3.68 |
| B:\BATCH26\3017BD4.FWA | 564.1287 | 201.0065 | 458.6025 | P | 5.09 |
| B:\BATCH26\TB0201A.FWA | 248.6455 | 277.2649 | 332.7476 | N | 2.10 |
| B:\BATCH26\TB0201B.FWA | 232.9224 | 391.4109 | 295.4229 | N | 1.35 |
| B:\BATCH26\TB0201C.FWA | 239.46 | 252.1328 | 300.8291 | N | 2.14 |
| B:\BATCH26\TB02021D.FWA | 258.6064 | 263.1091 | 344.29 | N | 2.29 |
| B:\BATCH26\TB0201E.FWA | 218.2578 | 246.2893 | 320.106 | N | 2.19 |
| B:\BATCH26\TB0201F.FWA | 239.6201 | 258.3145 | 345.2539 | N | 2.26 |
| B:\BATCH26\TB0201G.FWA | 247.1475 | 251.1152 | 338.1123 | N | 2.33 |
| B:\BATCH26\TB0201H.FWA | 258.2881 | 273.0261 | 360.0156 | N | 2.26 |
| B:\BATCH27\1082AB1.FWA | 385.5657 | 159.8253 | 326.0132 | P | 4.45 |
| B:\BATCH27\1082AB2.FWA | 414.3677 | 153.8197 | 331.4045 | P | 4.85 |
| B:\BATCH27\1082AB3.FWA | 479.1709 | 198.9961 | 394.8411 | P | 4.39 |
| B:\BATCH27\1082AB4.FWA | 570.894 | 185.8953 | 462.4937 | P | 5.56 |
| B:\BATCH27\1083AB1.FWA | 257.0143 | 122.054 | 181.8824 | P | 3.60 |
| B:\BATCH27\1083AB2.FWA | 210.7065 | 104.4279 | 142.7949 | P | 3.39 |
| B:\BATCH27\1083AB3.FWA | 309.1624 | 134.4028 | 242.1865 | P | 4.10 |
| B:\BATCH27\1083AB4.FWA | 423.1135 | 191.7181 | 302.8936 | P | 3.79 |
| B:\BATCH28\1029CE1.FWA | 155.9592 | 136.2709 | 128.425 | N | 2.09 |
| B:\BATCH28\1029CE2.FWA | 186.0649 | 147.7102 | 152.2537 | N | 2.29 |
| B:\BATCH28\1029CE3.FWA | 158.7642 | 225.14 | 250.0391 | N | 1.82 |
| B:\BATCH28\1029CE4.FWA | 79.57666 | 77.21307 | 60.0459 | N | 1.81 |
| B:\BATCH28\1081AC1.FWA | 140.2312 | 96.60205 | 136.459 | I | 2.86 |
| B:\BATCH28\1081AC2.FWA | 186.7627 | 157.9752 | 195.5107 | N | 2.42 |
| B:\BATCH28\1081AC3.FWA | 138.3887 | 144.9492 | 135.603 | N | 1.89 |
| B:\BATCH28\1081AC4.FWA | 164.5564 | 188.9536 | 177.8328 | N | 1.81 |
| B:\BATCH28\1081BC1.FWA | 134.3005 | 162.0945 | 147.7312 | N | 1.74 |
| B:\BATCH28\1081BC2.FWA | 177.1167 | 158.7465 | 186.1365 | N | 2.29 |
| B:\BATCH29\1002GH1.FWA | 288.0369 | 213.1395 | 326.9973 | I | 2.89 |
| B:\BATCH29\1002GH2.FWA | 385.2651 | 232.7882 | 415.4399 | I | 3.44 |
| B:\BATCH29\1002GH3.FWA | 360.0151 | 201.0891 | 373.9048 | P | 3.65 |
| B:\BATCH29\1002GH4.FWA | 348.5518 | 215.1918 | 380.9761 | I | 3.39 |
| B:\BATCH29\1002GH5.FWA | 167.1228 | 203.499 | 212.0437 | N | 1.86 |
| B:\BATCH29\1003FG1.FWA | 231.6809 | 176.5575 | 179.6406 | I | 2.33 |
| B:\BATCH29\1003FG2.FWA | 134.2655 | 138.4003 | 122.6637 | I | 1.86 |
| B:\BATCH29\1003FG3.FWA | 122.4147 | 138.8301 | 83.47949 | N | 1.48 |
| B:\BATCH29\1003FG4.FWA | 150.8757 | 161.2017 | 94.83154 | N | 1.52 |
| B:\BATCH29\1003FG5.FWA | 107.7399 | 118.4455 | 80.17358 | N | 1.59 |
| B:\BATCH29\1028FG1.FWA | 300.1177 | 142.48 | 237.3984 | P | 3.77 |
| B:\BATCH29\1028FG2.FWA | 325.6707 | 145.3931 | 244.9697 | P | 3.92 |
| B:\BATCH[illegible]1038DE.FWA | 176.2595 | 166.2288 | 153.6904 | N | [illegible] |



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|---|---|---|---|---|---|
| B:\BATCH29\1038DE2.FWA | 209.866 | 139.5973 | 165.6318 | I | 2.69 |
| B:\BATCH29\1038DE3.FWA | 86.95605 | 78.68304 | 74.06958 | N | 2.05 |
| B:\BATCH29\1038DE4.FWA | 154.6687 | 137.9493 | 138.5024 | N | 2.13 |
| B:\BATCH29\1084AC1.FWA | 346.9041 | 173.0016 | 310.8359 | P | 3.80 |
| B:\BATCH29\1084AC2.FWA | 192.3817 | 91.49591 | 127.8793 | P | 3.50 |
| B:\BATCH29\1084AC3.FWA | 158.4797 | 87.67383 | 107.7147 | P | 3.04 |
| B:\BATCH29\1088AB1.FWA | 304.8611 | 207.983 | 288.6938 | N | 2.85 |
| B:\BATCH29\1088AB2.FWA | 490.4385 | 214.1818 | 443.6851 | P | 4.36 |
| B:\BATCH29\1088AB3.FWA | 565.3447 | 289.0308 | 538.4463 | P | 3.82 |
| B:\BATCH29\1088AB4.FWA | 786.083 | 301.9977 | 696.228 | P | 4.91 |
| B:\BATCH29\1088AB5.FWA | 1164.748 | 341.0918 | 1032.968 | P | 6.44 |
| B:\BATCH29\1088AB6.FWA | 196.9912 | 239.2219 | 232.1235 | N | 1.79 |
| B:\BATCH29\1034FG1.FWA | 93.73132 | 98.97888 | 84.44397 | N | 1.80 |
| B:\BATCH29\1034FG2.FWA | 267.4011 | 135.9278 | 224.8438 | P | 3.62 |
| B:\BATCH29\1034FG3.FWA | 132.0311 | 93.4787 | 113.4548 | N | 2.63 |
| B:\BATCH29\1034FG4.FWA | 115.7614 | 92.74158 | 101.8497 | N | 2.35 |
| B:\BATCH29\1034FG5.FWA | 56.96765 | 71.97159 | 51.58514 | N | 1.51 |
| B:\BATCH29\1034FG6.FWA | 109.29 | 63.26291 | 100.7106 | I | 3.32 |
| B:\BATCH29\1031GH1.FWA | 89.08997 | 111.5498 | 90.34412 | N | 1.61 |
| B:\BATCH29\1031GH2.FWA | 118.6497 | 140.434 | 134.9961 | N | 1.81 |
| B:\BATCH29\1031GH3.FWA | 236.5916 | 137.0333 | 209.8811 | P | 3.26 |
| B:\BATCH29\1031GH4.FWA | 264.9988 | 84.66644 | 225.8915 | P | 5.80 |
| B:\BATCH29\1030EF1.FWA | 201.5256 | 152.8232 | 175.6736 | I | 2.47 |
| B:\BATCH29\1030EF2.FWA | 324.0381 | 173.8789 | 306.0352 | I | 3.62 |
| B:\BATCH29\1030EF3.FWA | 137.17 | 142.4705 | 127.1437 | N | 1.86 |
| B:\BATCH29\1030EF4.FWA | 118.0133 | 96.28448 | 89.27881 | N | 2.15 |
| B:\BATCH29\1039EF1.FWA | 512.0398 | 197.4965 | 465.9063 | P | 4.95 |
| B:\BATCH29\1039EF2.FWA | 297.0627 | 189.0717 | 306.9792 | N | 3.19 |
| B:\BATCH29\1039EF3.FWA | 374.5886 | 208.074 | 370.2505 | P | 3.58 |
| B:\BATCH29\1039EF4.FWA | 125.6692 | 194.2109 | 217.6301 | N | 1.77 |
| B:\BATCH29\1039EF5.FWA | 1301.214 | 242.016 | 1110.019 | P | 9.96 |
| B:\BATCH29\1036DE1.FWA | 256.0295 | 176.3595 | 279.4329 | N | 3.04 |
| B:\BATCH29\1036DE2.FWA | 147.2639 | 165.9941 | 197.1543 | N | 2.07 |
| B:\BATCH29\1036DE3.FWA | 499.7002 | 239.0521 | 478.8052 | P | 4.09 |
| B:\BATCH29\1036DE4.FWA | 314.1946 | 202.0052 | 343.8167 | I | 3.26 |
| B:\BATCH29\1036DE5.FWA | 662.5962 | 189.1163 | 580.145 | P | 6.57 |
| B:\BATCH29\1036DE6.FWA | 343.0566 | 172.1252 | 296.4905 | P | 3.72 |
| B:\BATCH30\3057CD1.FWA | 73.95129 | 91.84308 | 82.7002 | N | 1.71 |
| B:\BATCH30\3057CD2.FWA | 40.95215 | 146.0935 | 119.9075 | N | 1.10 |
| B:\BATCH30\3057CD3.FWA | 80.48389 | 38.76404 | 64.08801 | P | 3.73 |
| B:\BATCH30\3057CD4.FWA | 78.2749 | 87.99109 | 94.55127 | N | 1.96 |
| B:\BATCH30\7074BCA1.FWA | 109.946 | 101.4562 | 93.25037 | N | 2.00 |
| B:\BATCH30\7074BCA2.FWA | 276.2448 | 105.3469 | 196.3911 | P | 4.49 |
| B:\BATCH30\7074BCA3.FWA | 314.2827 | 118.6677 | 256.8861 | P | 4.81 |
| B:\BATCH30\7074BCA4.FWA | 187.17 | 118.2341 | 164.0062 | I | 2.97 |
| B:\BATCH30\7074BCA5.FWA | 112.8466 | 111.1658 | 94.31616 | N | 1.86 |
| B:\BATCH30\7074BCA6.FWA | 254.0393 | 142.1992 | 226.1565 | I | 3.38 |
| B:\BATCH30\7074BCA7.FWA | 78.41589 | 96.46558 | 83.67395 | N | 1.68 |
| B:\BATCH30\7074BCA8.FWA | 149.5558 | 137.3448 | 112.7821 | N | 1.91 |

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|---|---|---|---|---|---|
| B:\BATCH30\3072BC1.FWA | 2401.803 | 510.3644 | 2114.367 | P | 8.85 |
| B:\BATCH30\3072BC2.FWA | 690.9312 | 175.5476 | 551.7549 | P | 7.08 |
| B:\BATCH30\3072BC3.FWA | 369.978 | 179.5054 | 328.4197 | P | 3.89 |
| B:\BATCH30\3072BC4.FWA | 133.7639 | 118.3898 | 119.8461 | N | 2.14 |
| B:\BATCH30\3017BE1.FWA | 510.4692 | 233.5298 | 420.5005 | P | 3.99 |
| B:\BATCH30\3017BE2.FWA | 491.6948 | 235.4056 | 426.019 | P | 3.90 |
| B:\BATCH30\3017BE3.FWA | 462.8301 | 190.2977 | 361.2463 | P | 4.33 |
| B:\BATCH30\3017BE4.FWA | 328.2322 | 180.9901 | 271.626 | I | 3.31 |
| B:\BATCH30\3061BC1.FWA | 182.1318 | 91.18115 | 160.9114 | N | 3.76 |
| B:\BATCH30\3061BC2.FWA | 194.324 | 129.8593 | 184.6147 | N | 2.92 |
| B:\BATCH30\3043CD1.FWA | 137.2117 | 118.8567 | 126.5533 | N | 2.22 |
| B:\BATCH30\3043CD2.FWA | 102.9164 | 75.34546 | 66.18945 | N | 2.24 |
| B:\BATCH30\3043CD3.FWA | -172.456 | 167.3896 | 290.4717 | I | 0.71 |
| B:\BATCH30\3043CD4.FWA | 144.7544 | 193.1167 | 235.4866 | N | 1.97 |
| B:\BATCH30\1037EF1.FWA | 332.155 | 129.258 | 279.8909 | P | 4.74 |
| B:\BATCH30\1037EF2.FWA | 196.6191 | 129.1347 | 187.3735 | N | 2.97 |
| B:\BATCH30\1037EF3.FWA | 201.5222 | 134.7111 | 187.2903 | N | 2.89 |
| B:\BATCH30\1037EF4.FWA | 328.2051 | 148.2648 | 276.7585 | P | 4.08 |
| B:\BATCH31\1028GH1.FWA | 342.4294 | 141.2039 | 282.8804 | P | 4.43 |
| B:\BATCH31\1028GH2.FWA | 266.1521 | 185.4171 | 229.1094 | N | 2.67 |
| B:\BATCH31\1028GH3.FWA | 240.2378 | 181.1927 | 212.5513 | N | 2.50 |
| B:\BATCH31\1035EF1.FWA | 255.4775 | 201.8793 | 251.575 | N | 2.51 |
| B:\BATCH31\1035EF2.FWA | 375.491 | 183.9403 | 343.2375 | P | 3.91 |
| B:\BATCH31\1035EF3.FWA | 234.6812 | 229.6077 | 272.3726 | N | 2.21 |
| B:\BATCH31\1035EF4.FWA | 446.9609 | 232.6119 | 405.1982 | P | 3.66 |
| B:\BATCH31\1003GH1.FWA | 346.636 | 199.3074 | 270.218 | I | 3.09 |
| B:\BATCH31\1003GH2.FWA | 517.0356 | 226.0176 | 402.6484 | P | 4.07 |
| B:\BATCH31\1003GH3.FWA | 453.7129 | 242.8599 | 383.0317 | P | 3.45 |
| B:\BATCH31\1003GH4.FWA | 886.46 | 256.7068 | 718.7534 | P | 6.25 |
| B:\BATCH31\1003GH5.FWA | 343.05 | 220.6375 | 259.2654 | I | 2.73 |
| B:\BATCH31\1003GH6.FWA | 267.76 | 195.0668 | 204.4763 | N | 2.42 |
| B:\BATCH31\8053CD1.FWA | 185.6632 | 94.8623 | 149.5887 | N | 3.53 |
| B:\BATCH31\8053CD2.FWA | 82.62762 | 59.06924 | 57.3385 | N | 2.37 |
| B:\BATCH31\8053CD3.FWA | 191.0876 | 149.7065 | 179.9023 | N | 2.48 |
| B:\BATCH31\8053CD4.FWA | 225.6038 | 202.6721 | 191.3328 | N | 2.06 |
| B:\BATCH31\8053CD5.FWA | 127.0054 | 168.4392 | 169.2563 | N | 1.76 |
| B:\BATCH31\8054CD1.FWA | 66.58301 | 70.28394 | 50.30908 | N | 1.66 |
| B:\BATCH31\8054CD2.FWA | 45.29333 | 51.35056 | 33.29626 | N | 1.53 |
| B:\1034GH1.FWA | 537.8999 | 181.6792 | 452.0164 | P | 5.45 |
| B:\1034GH2.FWA | 698.397 | 232.4025 | 562.3467 | P | 5.42 |
| B:\1034GH3.FWA | 340.6741 | 141.5867 | 311.446 | P | 4.61 |
| B:\1034GH4.FWA | 454.3643 | 215.1498 | 405.5654 | P | 4.00 |
| B:\1087AB1.FWA | 28.66846 | 48.73544 | 39.63861 | N | 1.40 |
| B:\1087AB2.FWA | 113.7107 | 186.1545 | 108.8838 | N | 1.20 |
| B:\1087AB3.FWA | 53.43787 | 110.1939 | 54.45203 | N | 0.98 |
| B:\1087AB4.FWA | 48.71674 | 68.53915 | 47.02142 | N | 1.40 |
| B:\1087AB5.FWA | 56.80518 | 113.8398 | 61.61658 | N | 1.04 |
| B:\BATCH33\1002HI1.FWA | 1094.994 | 268.644 | 987.2334 | P | 7.75 |
| B:\BATCH33\1002HI2.FWA | 1459.111 | 310.8481 | 1213.092 | P | 8.60 |



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|---|---|---|---|---|---|
| B:\BATCH33\1002HI3.FWA | 989.3044 | 267.2383 | 904.7988 | P | 7.09 |
| B:\BATCH33\1089AB1.FWA | 284.3157 | 131.8722 | 181.5581 | I | 3.53 |
| B:\BATCH33\1089AB2.FWA | 487.2256 | 157.1935 | 412.2598 | P | 5.72 |
| B:\BATCH33\1089AB3.FWA | 193.9124 | 101.0941 | 152.5726 | I | 3.43 |
| B:\BATCH33\1031HI1.FWA | 111.3376 | 130.5643 | 116.9365 | N | 1.75 |
| B:\BATCH33\1031HI2.FWA | 135.7708 | 141.7064 | 126.2397 | N | 1.85 |
| B:\BATCH33\1031HI3.FWA | 87.80933 | 114.5443 | 96.01782 | N | 1.60 |
| B:\BATCH33\1038EF1.FWA | 171.3464 | 107.2909 | 130.3531 | I | 2.81 |
| B:\BATCH33\1038EF2.FWA | 298.5166 | 148.416 | 228.8284 | I | 3.55 |
| B:\BATCH33\1038EF3.FWA | 197.8389 | 129.7402 | 157.4307 | N | 2.74 |
| B:\BATCH33\7076AC1.FWA | 280.3165 | 88.70599 | 218.0975 | P | 5.62 |
| B:\BATCH33\7076AC2.FWA | 467.8928 | 177.6432 | 402.1206 | P | 4.90 |
| B:\BATCH33\7076AC3.FWA | 421.717 | 177.798 | 317.647 | P | 4.16 |
| B:\BATCH33\7077AC1.FWA | 281.5488 | 161.3992 | 304.751 | N | 3.63 |
| B:\BATCH33\7077AC2.FWA | 230.8252 | 159.1045 | 243.4626 | N | 2.98 |
| B:\BATCH33\7077AC3.FWA | 468.7351 | 175.926 | 427.6123 | P | 5.10 |
| B:\BATCH33\7077AC4.FWA | 263.1648 | 187.535 | 370.2681 | N | 3.38 |
| B:\BATCH33\7078AC1.FWA | 227.4229 | 115.8328 | 161.5026 | I | 3.36 |
| B:\BATCH33\7078AC2.FWA | 149.9196 | 95.61285 | 118.1549 | N | 2.80 |
| B:\BATCH33\7078AC3.FWA | 125.5741 | 97.83264 | 92.23376 | N | 2.23 |
| B:\BATCH33\7078AC4.FWA | 118.0247 | 104.1518 | 90.37866 | N | 2.00 |
| B:\BATCH33\7093AC1.FWA | 681.0662 | 222.1346 | 590.0881 | P | 5.72 |
| B:\BATCH33\7093AC2.FWA | 442.6426 | 202.9324 | 377.3225 | P | 4.04 |
| B:\BATCH33\7093AC3.FWA | 143.5054 | 160.6204 | 125.4983 | N | 1.67 |
| B:\BATCH34\1003HI1.FWA | 404.1343 | 193.8282 | 328.759 | P | 3.78 |
| B:\BATCH34\1003HI2.FWA | 177.6279 | 130.9216 | 132.5294 | N | 2.37 |
| B:\BATCH34\1003HI3.FWA | 260.4548 | 128.6822 | 183.2294 | P | 3.45 |
| B:\BATCH34\1003HI4.FWA | 144.299 | 86.26416 | 106.9904 | I | 2.91 |
| B:\BATCH34\1102AB1.FWA | 145.3094 | 103.2757 | 119.8682 | N | 2.57 |
| B:\BATCH34\1102AB2.FWA | 177.7573 | 153.6397 | 134.3401 | N | 2.03 |
| B:\BATCH34\1102AB3.FWA | 443.0605 | 202.8137 | 369.8467 | P | 4.01 |
| B:\BATCH34\1102AB4.FWA | 418.6792 | 183.9156 | 339.5583 | P | 4.12 |
| B:\BATCH34\1102AB5.FWA | 572.6631 | 203.4576 | 480.3716 | P | 5.18 |
| B:\BATCH34\1079BC1.FWA | 571.019 | 199.2367 | 463.9092 | P | 5.19 |
| B:\BATCH34\1079BC2.FWA | 391.5291 | 175.7438 | 343.7161 | P | 4.18 |
| B:\BATCH34\1079BC3.FWA | 349.9097 | 217.4825 | 350.4587 | I | 3.22 |
| B:\BATCH34\1079BC4.FWA | 509.4949 | 203.2496 | 463.908 | P | 4.79 |
| B:\BATCH34\1079BC5.FWA | 171.371 | 116.0129 | 146.5563 | N | 2.74 |
| B:\BATCH34\1007FG1.FWA | 203.2162 | 107.1407 | 167.0565 | P | 3.46 |
| B:\BATCH34\1007FG3.FWA | 131.5247 | 156.3177 | 136.3772 | N | 1.71 |
| B:\BATCH34\1007FG4.FWA | 145.2963 | 142.0886 | 109.1143 | N | 1.79 |
| B:\BATCH34\1007FG5.FWA | 123.8282 | 127.3762 | 120.7368 | N | 1.92 |
| B:\BATCH34\1006GH1.FWA | 117.0304 | 103.0318 | 104.6637 | N | 2.15 |
| B:\BATCH34\8053DE1.FWA | 75.05505 | 68.646 | 81.37207 | N | 2.28 |
| B:\BATCH34\8053DE2.FWA | 50.50391 | 47.03101 | 54.84521 | N | 2.24 |
| B:\BATCH34\8053DE3.FWA | 23.45831 | 40.17815 | 24.21661 | N | 1.19 |
| B:\BATCH34\8054DE.FWA | 236.2848 | 122.5695 | 215.8531 | P | 3.69 |
| B:\BATCH34\8054DE2.FWA | 151.5291 | 99.21368 | 136.1215 | N | 2.90 |
| B:\BATCH34\8054DE3.FWA | 64.94647 | 58.90787 | 52.74152 | N | 2.00 |

| | | | | | |
|---|---|---|---|---|---|
| B:\BATCH34\8054DE4.FWA | 78.56042 | 62.79971 | 55.2887 | N | 2.13 |
| B:\BATCH35\1005CD1.FWA | 267.155 | 165.9238 | 260.6421 | I | 3.18 |
| B:\BATCH35\1005CD2.FWA | 142.5601 | 144.5145 | 151.3914 | N | 2.03 |
| B:\BATCH35\1080CD1.FWA | 173.2861 | 165.3273 | 216.7788 | N | 2.36 |
| B:\BATCH35\1080CD2.FWA | 209.1868 | 129.1651 | 224.8772 | I | 3.36 |
| B:\BATCH35\1080CD3.FWA | 336.1375 | 215.1224 | 338.1753 | N | 3.13 |
| B:\BATCH35\1080CD4.FWA | 243.1907 | 144.0745 | 249.0581 | I | 3.42 |
| B:\BATCH35\1090AD1.FWA | 162.8999 | 160.5875 | 169.2939 | N | 2.07 |
| B:\BATCH35\1090AD2.FWA | 429.7991 | 150.1331 | 402.5963 | P | 5.54 |
| B:\BATCH35\1090AD3.FWA | 82.89197 | 74.19113 | 71.65405 | N | 2.08 |
| B:\BATCH35\1090AD4.FWA | 298.0247 | 127.3033 | 274.4254 | P | 4.50 |
| B:\BATCH35\1084BD.FWA | 485.0405 | 118.7142 | 341.9475 | P | 6.97 |
| B:\BATCH35\1030FG1.FWA | 142.9497 | 152.7587 | 132.8413 | N | 1.81 |
| B:\BATCH35\1030FG2.FWA | 77.64453 | 116.8467 | 78.89905 | N | 1.34 |
| B:\BATCH35\1030FG3.FWA | 95.94775 | 86.81573 | 94.00256 | N | 2.19 |
| B:\BATCH35\1030FG4.FWA | 107.5043 | 76.95721 | 80.31006 | N | 2.44 |
| B:\BATCH35\7075AC1.FWA | 154.8479 | 148.0179 | 118.0203 | N | 1.84 |
| B:\BATCH35\7075AC2.FWA | 525.0776 | 177.4279 | 406.4783 | P | 5.25 |
| B:\BATCH35\7075AC3.FWA | 215.2534 | 159.8837 | 193.5535 | N | 2.56 |
| B:\BATCH35\7075AC4.FWA | 301.4502 | 180.5428 | 227.0417 | I | 2.93 |
| B:\BATCH35\3057DE1.FWA | 42.80493 | 61.22647 | 59.85266 | N | 1.68 |
| B:\BATCH35\3057DE2.FWA | 30.22559 | 63.89752 | 50.2807 | N | 1.26 |
| B:\BATCH35\3057DE3.FWA | 35.79803 | 54.40134 | 51.40399 | N | 1.60 |
| B:\BATCH35\LOTIBLNK.FWA | 228.7563 | 232.3416 | 309.248 | N | 2.32 |
| B:\BATCH35\LOTIBLN2.FWA | 224.021 | 236.9841 | 288.853 | N | 2.16 |
| B:\BATCH36\7074CD1.FWA | 264.5775 | 109.485 | 213.6599 | P | 4.37 |
| B:\BATCH36\7074CD2.FWA | 244.2708 | 134.543 | 256.8721 | P | 3.72 |
| B:\BATCH36\7074CD3.FWA | 604.231 | 141.0889 | 483.448 | P | 7.71 |
| B:\BATCH36\7074CD4.FWA | 580.6057 | 153.9368 | 489.1047 | P | 6.95 |
| B:\BATCH36\7076CD1.FWA | 519.0244 | 186.0817 | 414.583 | P | 5.02 |
| B:\BATCH36\7076CD2.FWA | 323.7554 | 167.4814 | 268.9285 | P | 3.54 |
| B:\BATCH36\7076CD3.FWA | 555.8425 | 218.6017 | 447.627 | P | 4.59 |
| B:\BATCH36\7076CD4.FWA | 800.4688 | 252.0592 | 636.8926 | P | 5.70 |
| B:\BATCH36\7092AC1.FWA | 363.2539 | 161.8116 | 325.178 | P | 4.25 |
| B:\BATCH36\7092AC2.FWA | 211.3892 | 142.1649 | 188.5911 | N | 2.81 |
| B:\BATCH36\7092AC3.FWA | 423.3945 | 164.3154 | 391.3335 | P | 4.96 |
| B:\BATCH36\7092AC4.FWA | 252.5835 | 176.0345 | 266.2991 | N | 2.95 |
| B:\BATCH36\1039FG1.FWA | 417.249 | 121.4875 | 359.4001 | P | 6.39 |
| B:\BATCH36\1039FG1.FWA | 417.249 | 121.4875 | 359.4001 | P | 6.39 |
| B:\BATCH36\1039FG2.FWA | 124.7434 | 99.88354 | 107.0956 | N | 2.32 |
| B:\BATCH36\1039FG3.FWA | 241.8269 | 137.7694 | 249.2583 | I | 3.56 |
| B:\BATCH36\1039FG4.FWA | 321.97 | 121.8922 | 289.8455 | P | 5.02 |
| B:\BATCH37\3073BC1.FWA | 211.8101 | 192.1295 | 185.8093 | N | 2.07 |
| B:\BATCH37\3073BC2.FWA | 250.4399 | 212.6813 | 233.0493 | N | 2.27 |
| B:\BATCH37\3073BC3.FWA | 937.7622 | 232.5143 | 746.5469 | P | 7.24 |
| B:\BATCH37\3073BC4.FWA | 344.4531 | 197.5077 | 324.7114 | I | 3.39 |
| B:\BATCH37\3073BC5.FWA | 508.7683 | 200.4988 | 417.6226 | P | 4.62 |
| B:\BATCH37\3064CD1.FWA | 23.27631 | 23.47459 | 18.94742 | N | 1.80 |
| B:\BATCH38\1047DE1.FWA | 160.3925 | 108.1404 | 139.761 | N | 2.78 |



| | | | | | |
|---|---|---|---|---|---|
| B:\BATCH38\1047DE2.FWA | 281.6282 | 144.3744 | 222.8647 | I | 3.49 |
| B:\BATCH38\1047DE3.FWA | 125.3733 | 140.1495 | 122.9807 | N | 1.77 |
| B:\BATCH38\1047DE4.FWA | 242.8899 | 172.2131 | 208.2717 | N | 2.62 |
| B:\BATCH38\1037FG1.FWA | 245.5813 | 116.5233 | 212.9861 | I | 3.94 |
| B:\BATCH38\1037FG2.FWA | 540.3457 | 160.0994 | 455.282 | P | 6.22 |
| B:\BATCH38\1037FG3.FWA | 241.8967 | 112.9435 | 218.1243 | P | 4.07 |
| B:\BATCH38\1037FG4.FWA | 298.7668 | 123.4347 | 258.345 | P | 4.51 |
| B:\BATCH38\1069BD1.FWA | 174.554 | 88.13629 | 130.7842 | I | 3.46 |
| B:\BATCH38\1069BD2.FWA | 100.6733 | 91.50671 | 106.3143 | N | 2.26 |
| B:\BATCH38\1069BD3.FWA | 256.4508 | 84.60999 | 202.9794 | P | 5.43 |
| B:\BATCH38\1069BD4.FWA | 249.9238 | 82.78125 | 197.1167 | P | 5.40 |
| B:\BATCH38\1069CD1.FWA | 135.5411 | 81.13239 | 118.3679 | N | 3.13 |
| B:\BATCH38\1069CD2.FWA | 97.18555 | 119.2797 | 79.87561 | N | 1.48 |
| B:\BATCH38\1069CD3.FWA | 103.2305 | 101.8107 | 89.65063 | N | 1.89 |
| B:\BATCH38\1069CD4.FWA | 80.99329 | 89.62842 | 59.14771 | N | 1.56 |
| B:\BATCH38\7093CE1.FWA | 367.3247 | 238.3947 | 318.9307 | N | 2.88 |
| B:\BATCH38\7093CE2.FWA | 233.1418 | 227.8912 | 234.8044 | N | 2.05 |
| B:\BATCH38\7093CE3.FWA | 179.7078 | 203.8254 | 171.8899 | N | 1.72 |
| B:\BATCH38\7093CE4.FWA | 210.7327 | 185.8533 | 185.7297 | N | 2.13 |

# Optical Brighteners: Sorption Behavior, Detection, Septic System Tracer Applications

Steffan R. Fay[1], Ronald C. Spong[2], Scott C. Alexander[1], and E. Calvin Alexander, Jr[1].

ABSTRACT

Laboratory soil column experiments were used to evaluate the optical brighteners (fluorescent whitening agents) Tinopal[3] CBS-X (ASTM designation DSBP-1) and Tinopal[3] 5BM-GX (ASTM designation DASC-4) and the fluorescent dye eosin Y (C.I. 45380) as adsorbing tracers in subsurface systems. In a low organic carbon content glacial outwash sand (foc = 0.0034, 97% sand by weight) the solid-water distribution coefficient (Kd) was determined to be 0.26 cm^3/g for Tinopal CBS-X, 0.78 cm^3/g for Tinopal 5BM-GX, and 0.024 cm^3/g for eosin Y. All three compounds had simple sigmoidal breakthrough curves.

Optical brighteners can be detected in direct solution by fluorometry but suffer from interference associated with naturally occurring organic compounds. Unbrightened cotton can be used to qualitatively detect optical brighteners. Polyethersulfone filter media can be used to selectively remove optical brighteners from solution without changing the background fluorescence spectrum. The exposed filter medium can be analyzed as a solid sample in a scanning spectrofluorophotometer. The resulting spectrum can be used to measure the optical brightener concentration in the filtered sample. Polyethersulfone filters can be used to detect optical brighteners in samples collected in and around septic system drain fields at less than 1 ppb Tinopal 5BM-GX equivalent.

KEYWORDS

Optical brighteners, fluorescent whitening agents, detection systems, groundwater tracers, septic systems.

## INTRODUCTION

Fluorescent dyes are used extensively for tracing surface water and groundwater because of their low detection limits, ease and economy of detection, availability and safety. Fluorescent dyes have successfully been used to delineating otherwise unpredictable groundwater basins in karst environments (Quinlan and Ray, 1981; Alexander and others, 1993). Fluorescent dyes have also been used as adsorbing tracers in an effort to predict the breakthrough of pesticides in agricultural settings (Sabatini and Austin, 1991; Everts and Kanwar, 1994.)

Optical brighteners (also known as fluorescent whitening agents) absorb ultraviolet light and fluoresce in the blue region of the visible spectrum. The main commercial use of optical brighteners is in laundry detergents and textile finishing. Consequently, optical brighteners are relatively inexpensive and have been subjected to rigorous toxicity testing. Optical brighteners are found in domestic waste waters having a component of laundry effluent, and therefore can enter the subsurface environment as a result of ineffective sewage treatment. The potential exists to use optical brighteners as tracers of sewage effluent in polluted aquifers and as artificial tracers in pristine aquifers. In either case an understanding of the interaction between the dye and solid aquifer material is required to properly interpret tracer test results.

A great deal of information is available on the characteristics and behavior of the most frequently used dyes: rhodamine WT (RWT) and uranine C (URC) also known as fluorescein (Smart and Laidlaw, 1977; Everts and others, 1989; Shiau and others, 1993.)

This paper describes three aspects of our investigation into the potential use of optical brighteners as subsurface tracers. A soil column was used to compare the transport behavior of optical brighteners and the fluorescent dye eosin Y (EOS) to URC and RWT. We discuss a methodology for detecting optical brighteners on cotton using a scanning spectrofluorophotometer, and report the discovery and preliminary field results of a novel detection method utilizing polyethersulfone filter media.

Laboratory experiments were conducted with two stock optical brighteners supplied by the manufacturer. Both compounds are designed for use in domestic laundry detergent formulation at concentrations up to 0.5% on weight of formulation. Tinopal[3] CBS-X (TCBS) is a distyrylbiphenyl type whitener (see figure 1). TCBS is chlorine bleach stable in solution, has a high solubility (30% at 95C, 2.5% at 25C) and high fluorescence efficiency (Ciba, 1987). Tinopal 5BM-GX (T5BM) is a cyanuric chloride/diaminostilbene disulfonic acid derivative whitener (see figure 1). T5BM is beach stable only when sorbed to a substrate, is less soluble (1.5% at 50C) and has a lower fluorescence efficiency (Ciba, 1987). The optimal temperature range for sorption of both brighteners is in the 15C to 50C range.

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[3] Tinopal is a registered trademark of Ciba-Geigy Corporation, Greensboro, North Carolina, USA.

## SORPTION BEHAVIOR

Laboratory soil column experiments were conducted using a 30 cm (11.8 inch) long, 2.5 cm (1.0 inch) diameter borosilicate glass chromatography tube. Column end fittings and tubing were PTFE, with the exception of a silicone peristaltic pump drive section. The column was filled with repacked Rosemount Outwash aquifer material, obtained from a sand quarry near Coates, Minnesota. Column running parameters are listed in table 1. Organic carbon content was determined at the University of Minnesota Soil Science Research Analytical Laboratory. Column material grain size distribution was measured by standard sieve methods. Fines fraction was determined by inspection under an optical microscope. Hydraulic conductivity was calculated with the Hazen equation (see Freeze and Cherry, 1979, p. 350).

Table 1. Soil Column Parameters

| | | | |
|---|---|---|---|
| Column internal volume (cm^3) | 150 | Hydraulic conductivity by Hazen method (cm/s) | 1.4E-02 |
| Fraction organic carbon content, foc | 0.0034 | Porosity, n | 0.30 |
| Median grain size diameter, d50 (mm) | 0.34 | Repacked bulk dry density, ρb (g/cm^3) | 1.85 |
| Uniformity coefficient, d60/d10 | 2.8 | Pore water velocity (cm/h) | 30 |
| Sand: coarse, medium, fine (%) | 3, 37, 57 | Hydrodynamic dispersion coefficient, Dx (cm^2/h) | 3.4 |
| Fines: silt, clay (%) | 3, <1 | | |

Breakthrough data were collected in three separate column runs. The column was not repacked between runs. The breakthrough of a 1.0 g/L solution of sodium chloride (run #1) was used to calculate column parameters. Hydrodynamic dispersion coefficient, Dx was extracted from an analytical solution to the advection dispersion equation for saturated porous media (see Freeze and Cherry, 1979, p. 391) fitted to the chloride breakthrough curve. Chloride concentrations were determined by mercuric nitrate titration of column discharge aliquots. Approximately five pore volumes of water with no NaCl added were used to flush the column following run #1. Run #2 involved a 20+ pore volume continuous input of a mixture of URC, RWT and TCBS. Run #2 was followed by approximately 50 pore volumes of flushing. Run #3 was conducted using a continuous input of EOS and T5BM. Column runs were conducted in darkness or under subdued red lighting to minimize potential dye photodegradation, at approximately 25C.

Background ion concentrations have an effect on the transport characteristics of fluorescent dyes (Sabatini and Austin, 1991; Everts and Kanwar, 1994), so a pristine groundwater solvent was used in place of the traditional deionized water in an effort to more closely simulate field conditions. Groundwater was obtained from a flowing artesian well completed in the southern Minnesota Mount Simon aquifer. The water has previously been carbon-14 dated at over 10,000 years and contains no anthropogenic contaminants.

The fluorescent spectrum of the column discharge was monitored in the flow-through cell of a Shimadzu RF5000U scanning spectrofluorophotometer. Essential settings are listed in table 2. A synchronous scan mode was used at the detection wavelength separations (Δλ) listed. The relative dye concentration (C/Co) was determined from the area of characteristic peaks in the discharge fluorescence spectrum, e.g. C/Co(TCBS) = area of 440 nm peak in discharge / area of 440 nm peak in influent dye mixture (see figure 2.)

Table 2. Dye Properties

| Dye (ASTM designation / color index) | TCBS (DSBP-1) | T5BM (DASC-4) | URC (C.I. 45350) | RWT (Acid Red 388) | EOS (C.I. 45380) |
|---|---|---|---|---|---|
| Source | Ciba-Geigy | Ciba-Geigy | Fisher | Crompton Knowles | Fisher |
| Grade | commercial | commercial | purified | 20% solution | 88% powder |
| Batch # | 34918038 | 1009 | A-833 | 38 | 916991 |
| Concentration, Co (ppb) | 370 | 360 | 150 | 230 | 450 |
| Detection Δλ (nm) | 95 | 95 | 15 | 15 | 15 |
| Peak emission λ (nm) | 440 | 440 | 508 | 573 | 525 |
| Retardation factor, Rf | 2.6 | 5.8 | 1.04 | – | 1.15 |
| Kd (cm^3/g) | 0.26 | 0.78 | 0.006 | – | 0.024 |
| Koc (cm^3/g) | 76.5 | 229 | 1.76 | – | 7.06 |

Note: Peak emission wavelength and detection wavelength separation refer to analysis of direct solution samples.

Peak areas were calculated by integration of a best fit non-linear function. Figure 2 illustrates the Co concentration fluorescent spectra of all the dyes except T5BM, which has a shape identical to TCBS. Each symbol in figure 2 is a discrete data value in the fluorometer scan output. The black lines in figure 2 are the fitted curves from which areas were calculated, they do not just link the symbols. The peaks of URC, EOS and RWT were adequately described by a single peak function, with a linear or no background function. TCBS and T5BM were each described by a complex function made up of three simple peaks functions (not shown) superimposed on a small background peak (not shown). The subtraction of a background peak was required in the analysis for the optical brighteners to remove the effect of naturally occurring organic compounds which fluoresce in a similar region of the spectrum.

Retardation factors (Rf) were calculated as the number of pore volumes required to reach half influent concentration (C = Co/2). The solid-water distribution coefficient (Kd) was backed out of the expression Rf = 1 + (ρb / n ) . Kd, where n = porosity and ρb = bulk density. The organic carbon-water distribution coefficient (Koc) was calculated from the expression Koc = Kd / foc, where foc = fraction organic carbon in the aquifer material.

Figure 1. Chemical Structures of Dyes

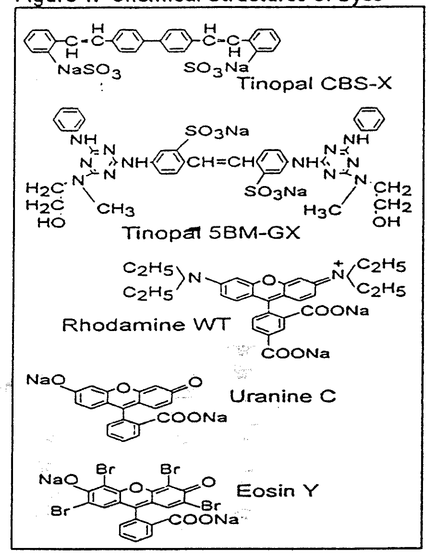
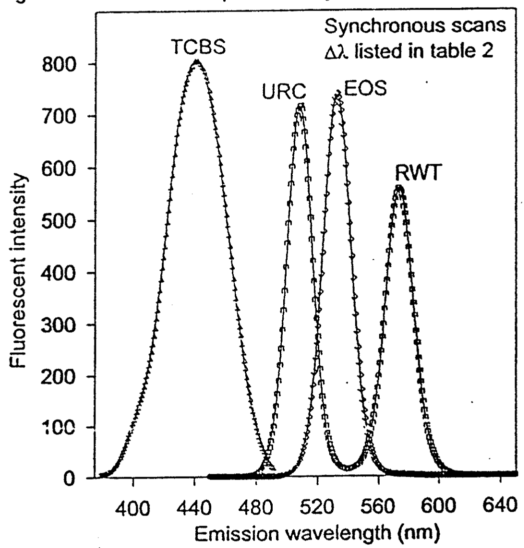



Figure 2. Fluorescent Spectra of Dyes




## Results

Figure 3 summarizes the column experiment results. Each symbol in figure 3 represents a discrete data point derived from a single fluorometer scan. Chloride breakthrough exhibited the normal sigmoidal shape characteristic of saturated flow in a relatively homogenous porous medium, reaching C = Co/2 at 1.0 pore volumes. URC and EOS where the earliest dyes to breakthrough, both reaching C = Co/2 within 1.2 pore volumes. Optical brighteners were significantly retarded. RWT showed the characteristic stepped breakthrough attributed by Sabatini and Austin (1991) and Shiau and others (1993) to differing transport properties of two RWT structural isomers.

Retardation factors and distribution coefficients are listed in table 2. The complex breakthrough curve of RWT precludes the calculation of a single, meaningful value for its Rf, Kd and Koc. An additional column experiment using a 1.0 pore volume input followed by flushing showed that sorption of TCBS to aquifer material is reversible. Over 94% of input dye mass was recovered within 15 pore volumes of flushing (results not shown).

The Kd values obtained for URC from this experiment are approximately 1 order of magnitude lower than the results of Sabatini and Austin, 1991 (Kd = 0.05 cm^3/g) who used a very similar apparatus, porous medium and method. The source of this discrepancy is being investigated.

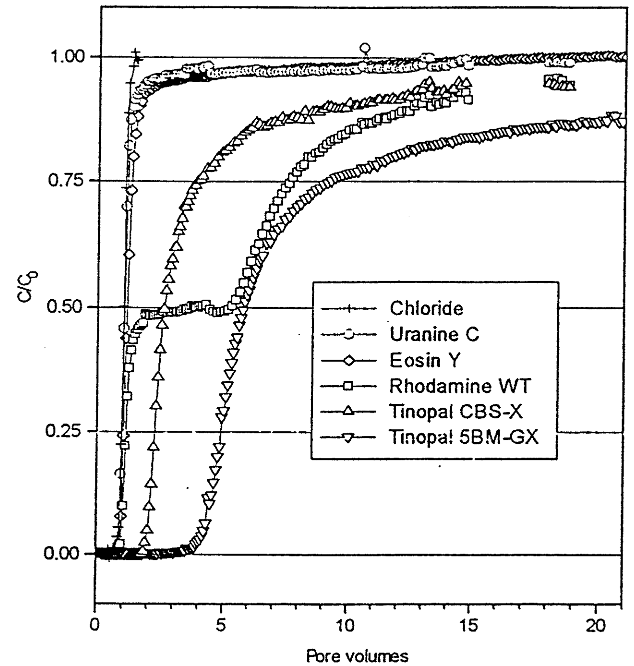
## Conclusions

The breakthrough curve for EOS in this experiment was almost identical to that of URC. The symmetrical substitution of four Br atoms for four H atoms on the URC structure (see figure 1) does not appear to significantly affect the molecule's adsorption properties. EOS appears to be a good alternative to URC for tracer applications where retention on aquifer material is undesirable. EOS has the benefit of having a peak fluorescence emission wavelength higher than that of URC (see table 2 and figure 2). This characteristic reduces the potential for interference with naturally occurring fluorescent compound which tend to be concentrated at shorter green and blue wavelengths.

As stated by earlier authors, interpretation of RWT tracer test results requires an appreciation for its complex breakthrough pattern. In the absence of other tracer data the double stepped breakthrough of RWT could be misinterpreted as being indicative of multiple dye pathways.

TCBS and T5BM are potentially useful tracers. Although the detection of both dyes is subject to interference from other compounds, analytical developments can remedy that problem. A promising analytical improvement is discussed later in this paper. TCBS and T5BM are not distinguishable fluorometrically, ruling out their concurrent use. However, their simple sigmoidal breakthrough curve and differing retardation factors means that they could be used for predicting the breakthrough of various retarded contaminants, with perhaps less ambiguity than RWT. The strong sorption characteristics of optical brighteners improves their utility as indicators of failing septic systems where the soil adsorption property may have broken down.

Figure 3. Soil Column Experiment Results Summary




## COTTON DETECTION SYSTEM

While optical brighteners are readily detectable by fluorometry at the part per billion level in laboratory prepared solutions, problems exist with extending this method of analysis to field samples. A primary cause for concern is the presence of variable concentrations of naturally occurring organic compounds which fluoresce at similar wavelengths to optical brighteners in solution. Figure 4 is a synchronous fluorometer scan (Δλ = 95 nm) which shows the spectra of both a pristine groundwater and a dilute solution of T5BM. These complications lead Alhajjar and others (1990) to conclude that optical brighteners are not suitable indicators of septic system impact on groundwater. These authors' limitation of their optical brightener data to filter fluorometer analyses on direct water samples demonstrated the ineffectiveness of wide-band groundwater fluorescence. Their work does not, as they assert, indicate that optical brighteners can not be used as tracers of septic system effluent.

Aley (1985) successfully used a detection system based on unbrightened cotton to identify sewage impacts on karst groundwater. Quinlan (1981) used optical brighteners as artificial tracers employing a similar cotton based detection system. The use of cotton detectors exploits the strong sorption affinity of optical brighteners for cotton. We are currently using a spectrofluorophotometer to analyze cotton detectors as part of a regional survey of septic system impact on domestic wells in southern Minnesota described by Spong and others (1995, this publication.)

The application of a dilute solution of T5BM to unbrightened cotton produces a characteristic peak in the fluorescence spectrum of the material at approximately 440 nm. Figure 5 is a synchronous fluorometer scan (Δλ = 60 nm) which shows the spectra of unbrightened cotton and cotton doped with a dilute solution of T5BM. Note that the sharp peak at approximately 415 nm is present in both signals. TCBS and powder and liquid formulation domestic laundry detergents produced identical results (not shown). The cotton detection system is based on the recognition of the characteristic peak in the cotton spectrum at 440 nm after exposure of the cotton to waters containing optical brighteners. A sample is considered positive for optical brighteners when the characteristic peak is present.

Figure 4. T5BM Detection in Direct Solution

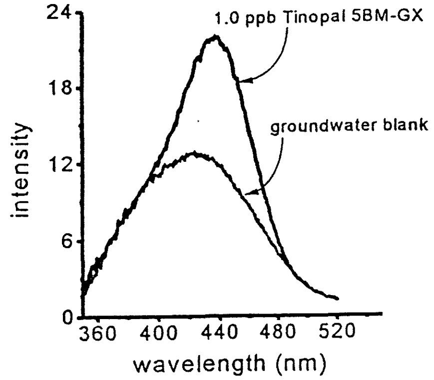
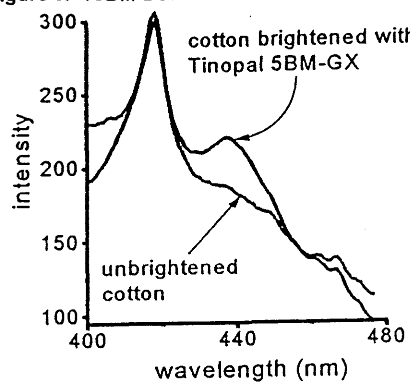



Figure 5. T5BM Detection on Cotton

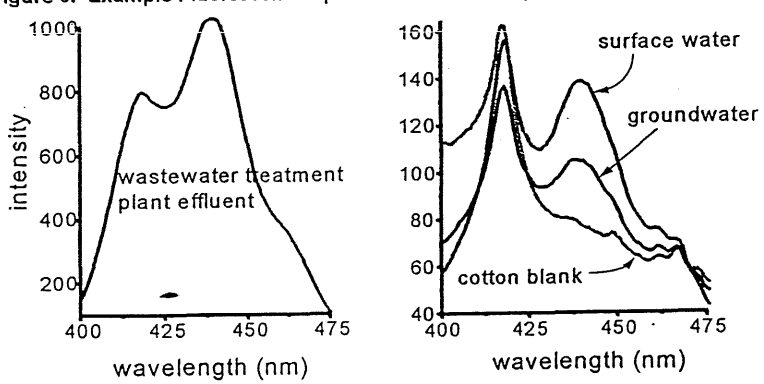



## Results

Optical brighteners have been detected in a variety of water environments. Spong and others (1995, this publication) summarize the results of a regional survey of optical brighteners in shallow water table aquifers. Figure 6 contains some typical positive sample scans. All of the spectra in figure 6 are synchronous scans ($\Delta\lambda$ = 60 nm) of cotton samples. Note that the graph on the left side of figure 6 (cotton after exposure to the effluent stream of a waste water treatment plant) has a much larger y axis, indicating a greater degree of brightening.

Long term exposure of the cotton to a supply of the sample water (of the order of weeks) is typically required (see Spong and others, 1995). While increasing exposure time improves the chance of detection by allowing more of the sample water supply to encounter the cotton detector problems arise with bacterial colonization, mineral precipitation and cotton fiber loss. These phenomena tend to lead to heterogeneous brightening of the cotton surface, requiring multiple scans of various parts of each sample and restricting the cotton detection method to a qualitative positive/negative determination.

Figure 6. Example Fluorescence Spectra of Cotton Samples Positive for Optical Brighteners




## NOVEL POLYETHERSULFONE DETECTION SYSTEM

This section of the paper describes our investigation into an improved detection methodology for optical brighteners. Syringe tip filter capsules are frequently used to remove suspended solids in the preparation of water samples for dissolved species analysis. One material used in the construction of such filters is polyethersulfone (PES). PES filters appear to selectively absorb optical brighteners.

The Acrodisc[4] (AD) and Acrodisc PF (ADPF) products both use PES as a filtration medium. Both products are housed in a 25 mm diameter modified acrylic housing, having an effective filtration area of 2.8 cm^2 (Gelman, 1994). The AD model that we tested has a 0.45 µm PES filter. We also used the ADPF which utilizes a 0.2 µm PES filter preceded by a 0.8 µm PES prefilter. Our investigation of the AD and ADPF filters consisted of three separate series of experiments:

***Experiment #1 (Dye scavenging efficiency of PES):*** Dye solution mixtures used for earlier column experiments (see table 2) were used to test the degree to which PES filters remove fluorescent dyes and optical brighteners from solution. In each experiment 3 ml of dye mixture solution was forced through an AD filter with a single-use 3 ml syringe directly into a 3 ml acrylic fluorometer cuvette. A 1 ml air purge was used, in accordance with the filter manufacturer's instructions, to remove liquid held on the filter by surface tension. The solution which had passed through the PES filter was analyzed and compared with an unfiltered (U) dye sample. The method of dye solution analysis was identical to that described in the "sorption behavior" section, above. To investigate the effect of filtration through an inert medium a 1.0 µm pore size glass fiber (GF) filter was also evaluated. Each dye/filter combination was tested in triplicate.

***Experiment #2 (Relationship between sorbed mass and fluorescence):*** The solid sample holder of the fluorometer allows the analysis of materials such as the PES filter medium. In a series of experiments a known mass of dye was applied to individual ADPFs using the syringe method described above, with the addition of a 9 ml deionized water rinse. After exposure the filter casing was broken open, and the filter medium removed. The fluorescent emission spectrum of the filter medium was measured between 380 nm and 525 nm, holding an excitation wavelength of 370 nm. Five samples were examined for photodegradation during analysis. After an initial scan samples were allowed to remain in the path of the fluorometer excitation beam (set at 650 nm) for approximately 2 minutes, and then reanalyzed. This time frame brackets the normal period which would be allowed to lapse between placing the sample in the fluorometer and initiating the emission scan.

***Experiment #3 (Effect of natural background organic compounds):*** A sample of lake water containing no optical brighteners, but relatively rich in natural organic compounds was filtered through ADPF. This experiment was conducted to measure the degree to which naturally occurring organic compounds might adhere to the PES medium and interfere with optical brightener detection.

## Results

Figure 7 graphically displays the results of experiment 1. The x axis reflects the three treatments given the dye mixtures: unfiltered (U), glass fiber filtered (GF) or polyethersulfone filtered (PES). The connecting lines are a visualization aid only and have no physical interpretation. Box height at each x axis interval indicates the variability encountered in triplicate analyses. Figure 7 shows that while over 80% of both optical brighteners passed through the GF filter no TCBS or T5BM was detectable after passing through the PES filter. URC and RWT concentrations were slightly reduced by PES filtration. EOS was reduced to approximately 40% of unfiltered concentration. The GF filtered URC samples had an apparent concentration of 105% relative to unfiltered samples. This is possibly due to the removal of iron colloids and/or microscopic calcite laths. These particles were observed in the unfiltered groundwater and may slightly obscure the fluorescence of unfiltered direct dye samples.

Figure 7. Sorption to Filter Media

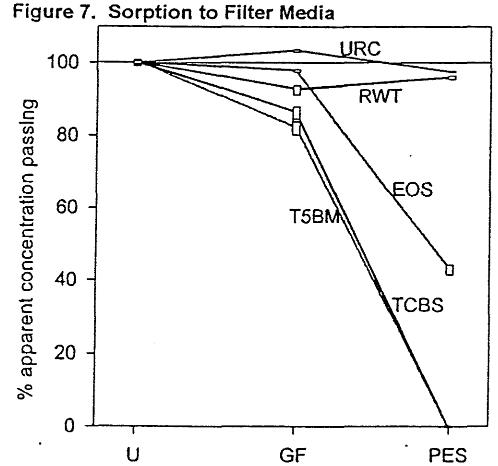



Figure 8. Tinopal 5BM-GX on Polyethersulfone

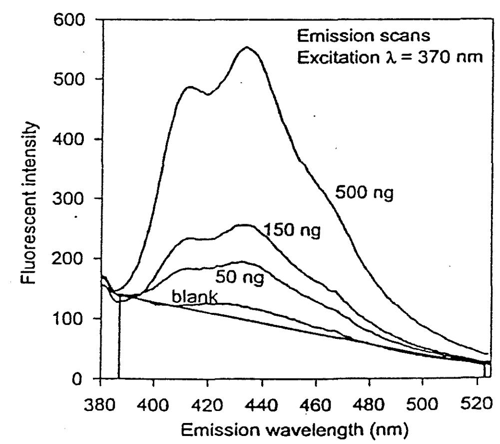



Figure 8 contains the fluorescence spectra of PES media with various masses of T5BM sorbed. A double peaked signal, which increases in area with increased sorbed dye mass, is evident. The main peak is at 434 nm with a secondary peak at 414 nm.

Figure 9 is a plot of emission scan peak area versus sorbed mass for TCBS and T5BM. Peak area was calculated by numerical integration of the fluorometric emission scan signal between 388 nm and 525 nm followed

[4] Acrodisc and Acrodisc PF are registered trademarks of Gelman Corporation, Ann Arbor, Michigan, USA.

by the subtraction of the underlying trapezoid (see fig. 8). The complex nature of solid phase fluorescence spectra precluded area integration with the non-linear curve fitting procedure described above for direct solution analysis. The linear best fit for T5BM is described by the function: **mass (ng) = [peak area (fluorescent intensity . nm) - 667.9] / 55.18**. The constant in this equation (667.9) represents the best estimate of the portion of the peak area attributed to unexposed "blank" PES.

In figure 9 vertical lines connect samples which were analyzed immediately and those which were allowed to remain the fluorometer excitation beam. Significant photodegradation is evident for T5BM, especially at higher concentrations. No degradation was observed for TCBS. The TCBS curve is steeper than the T5BM indicating more media brightening per mass of brightener sorbed. These observations are in accordance with the manufactures specifications.

Figure 10 summarizes the results of experiment #3. The lower box compares the emission scan spectra of the organic rich lake water before and after it was passed through the PES filter. The fluorescent signature is essentially unchanged which indicates no significant removal of fluorescent compounds by the filter. Note that the vertical scale of the lower part of figure 10 is much more expanded than that of figure 8 or the upper part of figure 10. The upper box compares the emission spectra of two PES filters, one exposed to the lake water and the other to deionized water. The lake water produced no significant enhancement on the PES filter compared to organic free deionized water. The same experiment comparing optical brightener free groundwater with deionized water produced identical results (not shown.)

**Figure 9. Tinopal Calibration Curves**

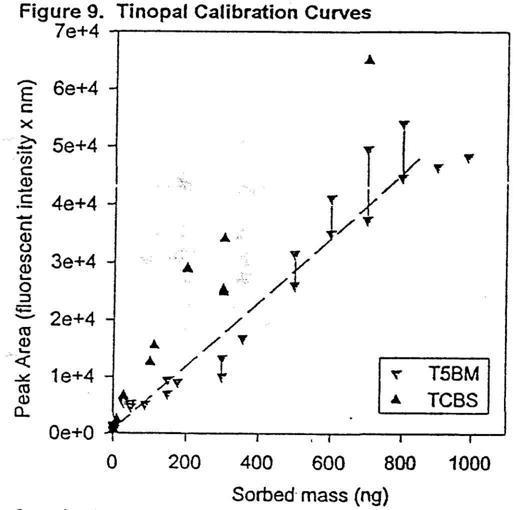
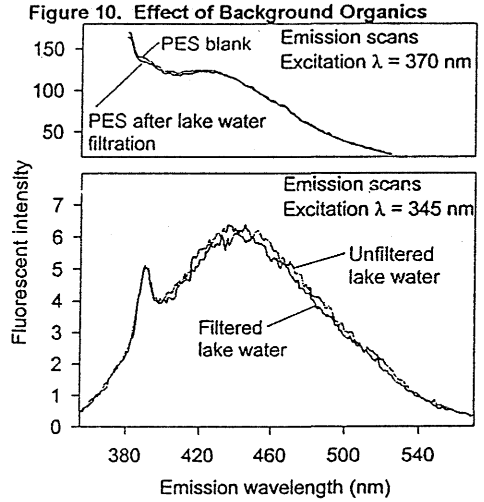



**Figure 10. Effect of Background Organics**




## Conclusions

PES filters quantitatively sorb optical brighteners from solution without simultaneously sorbing at least some naturally occurring organic compounds. We speculate that the mechanism responsible for the binding of optical brighteners to PES is related to the sulfonate functional groups present on both Tinopal compounds (see figure 1). T5BM is prone to photodegradation during fluorometric analysis when sorbed to the PES medium at higher concentrations. The phenomenon appears to be less important at lower concentrations.

Naturally occurring organic compounds in a lake water and groundwater sample did not interfere with optical brightener detection using PES filter media.

## SEPTIC SYSTEM TRACER APPLICATIONS

The detection methodology described above was used to analyze samples obtained from two instrumented septic systems located in rural southern Minnesota. The systems, identified here as A and B, were constructed in October, 1994 in heavy clay-till soils where shallow water table conditions generally prevail. Both systems are equipped with a curtain tile to locally depress the water table beneath the drain field. The system A drain field is situated in a topographically flat area. System B has a gravity fed drain field installed on a moderate slope. Both systems receive input from single family dwellings.

Water quality in and around the drain field is sampled through a series of lysimeters located at 30.5 cm, 61 cm and 91.5 cm (1, 2 and 3 feet) below the drain field pipes. Additional samples were obtained from the drain field influent. The optical brightener data discussed below come from a single sample set collected March 27, 1995. Other water qualit[illegible]ieters were recorded but are not discussed here.

For each sample between 36 ml and 72 ml of water were passed through and ADPF in the field. Filters were refrigerated in darkness until being broken apart and having the PES filter medium subjected to fluorometric analysis. Fluorometric spectra with discernible peaks in the region characteristic of optical brighteners were analyzed by the methodology described above. Peak areas were converted to an equivalent T5BM mass with the linear regression formula. Sorbed mass was converted to concentration based on known sample volume.

## Results

Peaks were visually noted to be very similar in shape to the T5BM emission signatures (fig. 8.) Optical brighteners were detected in five of the six lysimeter samples and one of the two septic system influent samples (see table 3.) The practical detection limit appears to be approximately 0.1 ppb T5BM equivalent, corresponding to the smallest discernible peak in the sample emission spectra of this sample set. The very brief presentation of this field data is used only to demonstrate that optical brighteners can be detected in field situations by the methodology outlined above. This technique is a component of ongoing research at these and other instrumented septic systems.

**Table 3. Optical Brightener Concentrations (ppb T5BM equivalent)**

| System | Influent | 30.5 cm | 61 cm | 91.5 cm |
|---|---|---|---|---|
| A | 8.4 | 0.3 | 1.6 | 3.2 |
| B | <0.1 | <0.1 | 0.8 | 0.1 |

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ATTACHMENT 3.

# OPTICAL BRIGHTENER SCREENING FOR SEWAGE CONTAMINATION OF WATER TABLE AQUIFERS IN SOUTHEASTERN MINNESOTA, USA

Ronald C. Spong[1], Steffan R. Fay[2] and E. Calvin Alexander, Jr.[2]

## ABSTRACT

Novel screening methods for detecting optical brighteners, fluorescent organic blue dyes principally used in laundry detergents for whitening fabrics, have been developed for the monitoring of water table aquifers impacted by septic systems. Four rural residential communities characterized by private water supply and sewage systems were selected in southeastern Minnesota. Developments were chosen with a variety of saturated and unsaturated zone materials and thicknesses, water table and well depths, and topographic and cultural settings. Sampling sites were enrolled if wells were completed above regional aquitards. Sanitary surveys of sampling sites were completed with attention to drinking water usage and waste/wastewater disposal practices to uncover sources of cross-contamination. Water supplies were sampled and analyzed to determine aquifer sources, sanitary quality and natural backgrounds and anthropomorphic contributions of physicochemical and microbiological parameters of interest (e.g., nitrate, chloride and coliform bacteria). Filter holders containing untreated cotton, activated carbon and polysulfone/polyethersulfone membrane filters were installed as immersion-type detectors in toilet reservoirs. Syringe filter capsules comprised of polyethersulfone membranes were utilized for direct sampling. Exposure times ranged from minutes to months, and exposed filter media were analyzed in solid phase utilizing a scanning spectrofluorophotometer. Spectral data were computer-processed to objectively match peaks with the spectra obtained from pure fluorescent dyes and laundry detergent formulations. Detections were positive if matched peaks at 440 nm appeared above background fluorescence. Water supply test data and site survey information indicative of septic system contamination were moderately correlated with positive optical brightener detections.

## KEY WORDS

Fluorescent whitening agents (FWA) or optical brighteners; groundwater contamination; septic systems or on-site sewage systems; and water table aquifers.

## INTRODUCTION

Septic systems and other waste and wastewater disposal practices account for a significant share of the nonpoint source pollution that directly and indirectly impacts the burgeoning rural and urban unsewered communities in Minnesota which are largely dependent on groundwater resources for drinking water supplies (MPCA, 1989). Many quantitative contaminants, such as nitrate which has a natural background concentration less than 1.0 mg N/L in regional groundwaters, have potentially several sources. Therefore, it is difficult to assign responsibility for the impacts, target timely and effective remediation and facilitate land use planning and education to prevent and mitigate the pollution. This is especially true in agricultural settings where, for example, nitrogen from fertilizers and livestock operations is practically indistinguishable from septic system nitrogen.

Traditional sanitary indicators of drinking water supplies, such as coliform bacteria and nitrate, are ambiguous, especially if test results are variable, at or below background levels or negative. Straining, adsorption and competition limit fecal bacteria migration and survival, and reducing or denitrifying conditions either slow nitrogen oxidation to nitrate or reverse it (Bitton and Gerba, 1984). Negative sanitary tests alone do not prove that a water supply is safe for human consumption without more extensive testing. Other quantitative pollution parameters indicative of septic system contamination, including electrical or specific conductance and chloride, give similar equivocal results. Therefore, septic system-specific, qualitative contaminants (i.e., with no natural background concentrations in groundwaters), such as surfactants (MBAS - methylene blue active substances, etc.) and optical brighteners, also known as fluorescent whitening agents (FWA), have been investigated as septic system indicators.

Synthethic optical brighteners were developed in the 1930's by organic chemists after Krais in 1929 isolated aesculin (a glucosidal derivative of coumarin) from horse chestnuts which temporarily brightened linen (Zahradnik, 1982). Following World War II, additional optical brighteners, derived from DASC (diaminostilbene/cyanuric chloride), DSBP (distyrylbiphenyl) and other aromatic hydrocarbons, were synthesized and found widespread commercial application. Use in detergent compounds for whitening fabrics, especially cotton, accounts for approximately 80 percent of the optical brighteners produced annually in the United States.

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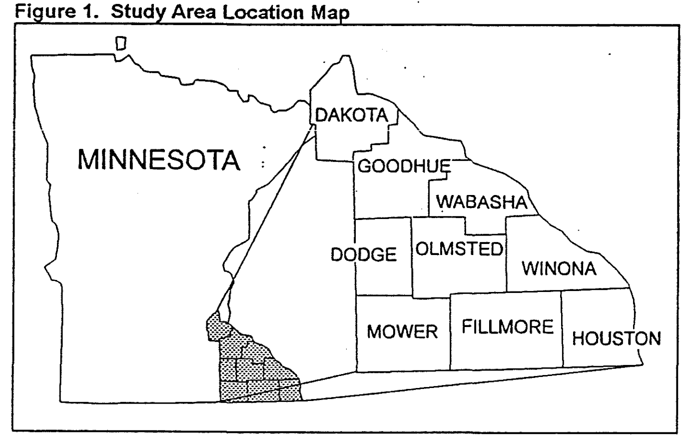
Optical brighteners comprise between 0.1 and 2 percent by weight of modern laundry product formulations (average range of 0.2-0.5 percent). In Minnesota, non-commercial phosphate detergents were banned in 1970 to slow the progressive eutrophication of the State's valuable recreational surface water resources. Synthetic detergent compounds, such as linear alkyl sulfonates, were substituted but first met with dissatisfaction because of "dingy", "dull" looking, washed clothing. Manufacturers responded by adding higher concentrations of optical brighteners to enhance the appearance. Consequently, optical brighteners have been discharged to septic systems for 25 years and have been detected in surface and ground waters in southeastern Minnesota (Spong, 1993).

Since the mid-1970's, interest in optical brighteners or fluorescent whitening agents (FWA) as passive tracers of septic system contamination of groundwaters has been pursued by researchers with varied results. Kerfoot and Brainard (1978) recommended optical brighteners as indicators of septic system pollution which eventually led to the commercial development of instruments known as "Septic Leachate Detectors" or "Septic Snoopers". The instruments combined a filter fluorometer with a specific conductivity meter and were used in Clean Water Act-funded lake pollution and restoration studies in the late 1970's through the mid-1980's. However, their reliability and specificity were debated when studies of fluorescent, dissolved organic carbon compounds (FDOC), including natural humic and fulvic acids, suggested significant interferences (Carlson and Shapiro, 1981).

Alhajjar, et al (1990) reported in a study of seventeen residential septic systems in central Wisconsin that optical brighteners were unsatisfactory as indicators of shallow aquifer sewage contamination. Utilizing upgradient and downgradient drivepoints for sampling and filter fluorometry for FWA analysis of aqueous samples, they reasoned that the undetectable optical brighteners were decomposing or sorbing to soil. They found that dissolved solids (detected as specific conductance) moved through the soil, and chloride was cited as the most reliable sewage indicator. However, use of non-chlorine bleach-stable DASC optical brighteners, well placement and sampling, aqueous sample filter fluorometry and FDOC interference may account for the lack of FWA detections.

Optical brighteners are reliable tracers in karst hydrogeologic investigations despite FDOC interefences and dye costs (Smart and Laidlaw, 1977; Aley, 1985; Alexander and Quinlan, 1992). Fay, et al, (this publication) describe the use of scanning spectrofluorophotometry for solid phase detection of optical brighteners and other fluorescent dyes. Such advances in selective filter media adsorption, fluorometric technology and procedures and the computer processing of resulting spectral data address concerns of low and variable optical brightener concentrations, interfering background fluoresence and subjective data evaluation appearing in the literature.

**Figure 1. Study Area Location Map**




## METHODS AND MATERIALS

### *Site Selection, Evaluation and Sampling*

This Minnesota Legislature-approved research project (Spong, 1993) encompasses a nine-county area of southeastern Minnesota (Figure 1.), and the four communities selected represent a variety of cultural, topographic and hydrogeologic settings (Table 1.) with which to test the hypothesis that optical brighteners selectively sorbed to cotton, other cellulosic fibers and selective filter media can be reliable qualitative and, perhaps, semi-quantitative indicators of septic system contamination of groundwaters. The villages of Castle Rock, Coates, Empire City and Vasa are rural residential communities comprised of urban laborers and local agribusiness, service industry and retired persons. All are characterized by early 1900's structures, limited road and drainage improvements and pre-Code wells and septic systems. New buildings, wells, septic systems and other enhancements occur infrequently.

Older residences were chosen for the project primarily because they were served by wells completed in surficial, unconfined aquifers above regional aquitards. Participation in the project was voluntary and required access for sampling and a brief survey. An average of 75 percent of those solicited declined to participate which limited site selection in most communities. Once selected, participants were interviewed about a number of residential living habits, knowledge of their wells, septic systems and other practices, general health and concerns. Sanitary surveys were conducted of the wells and water supplies, septic systems and other waste and wastewater disposal devices with particular attention to potential cross-contamination.

Filter holders were secured in the reservoirs of the most used toilet in buildings, and water supplies were sampled and analyzed in the field and laboratory. Owners were apprised of test results and any recommendations if problems were observed. Filter holders were retrieved and replaced periodically, and water supplies were resampled to help resolve certain problems (e.g., coliform bacteria present).

Table 1. Cultural, Topographic, Geomorphic and Hydrogeologic Features of Four Communities

| Feature | Castle Rock | Coates | Empire City | Vasa |
|---|---|---|---|---|
| County (area) | Dakota (southwest) | Dakota (north) | Dakota (central) | Goodhue (north) |
| Occupied Buildings | 67(7 nonresidential) | 62(5 nonresidential) | 57(2 nonresidential) | 43(7 nonresidential) |
| Polygonal Area | 121 ha (299 acres) | 65 ha (160 acres) | 19 ha (47 acres) | 53 ha (130 acres) |
| Vertical Relief | 9 m (29.5 ft) | 7 m (23 ft) | 4 m (13 ft) | 21 m (69 ft) |
| Slope (% gradient) | 0% ~ 6% | 1% ~ 6% | 0% ~ 2% | 2% ~ 12% |
| Soils | loam, silty loam (cl) | silty to sandy loam | loam to loamy sand | silty loam to loam |
| Geomorphology | pre-Qw morraine - outwash plain | loess-mantled Qw outwash plain | buried bdrk valley alluvial/Qw outwash | loess-mantled pre-Qw till |
| Surficial Bedrock | rsdl ss, dolostone | rsdl ss, dolostone | dolostone | rsdl ss, dolostone |
| Bedrock Depth | 3-14 m (9-46 ft) | 15-27 m (50-90 ft) | 3-91m (10-300 ft) | 1-15 m (3-50 ft) |
| Water Table Depth | 3-12 m (10-40 ft) | 21-27 m (70-90 ft) | 3-12 m (10-40 ft) | 12-18 m (40-60 ft) |
| Shallow Well Depth | Drivepoints 6-9 m Drilled wells 12-55m | Drilled wells 21-61m | Drivepoints 6-9 m Drilled wells 12-46m | Drilled wells 18-76m |
| Shallow Aquifer Flow | East-southeast | Northeast | Northeast | North-northeast |

*NB: ha = hectares; m = meters; ft = feet; cl = clay loam; Qw = Wisconsinan; rsdl ss = residual sandstone*

***Optical Brightener Filter Media, Sampling and Analysis***

Immersion filter holders were constructed of fine-mesh, black fiberglas window screening which was distilled water-rinsed, folded and stapled to form separate compartments for the filter media and channels for plastic tywraps that were used to secure filter holders to the toilets' standpipes. Filter media included untreated cotton facial pads (Target and Johnson & Johnson brands), activated carbon (Fisher Scientific: 6-14 mesh) and polysulfone/polyethersulfone 0.45 um-pore membrane filters (Gelman Science: trademarks "Tuffryn", "Supor", "Biotrace" and "UltraBind"). Precautions were taken to isolate the filter media and holder materials from possible optical brightener contamination. Completed holders and filter media were tracked as lots, randomly sampled and analyzed as "blanks" to control for false positives. If a blank tested positive, the entire lot was discarded.

In place of direct aqueous samples where FDOC interference significantly limits detection of very low optical brightener concentrations in groundwaters, cotton was selected due to its success in karst water tracing studies (Aley, 1985; Alexander and Quinlan, 1992). Side-by-side comparisons were run with cotton and activated carbon, the latter being a non-selective FDOC adsorption medium. Cotton was found to be largely uneffected by FDOC adsorption. However, solid phase fluorometric analysis of cotton blanks consistently found a characteristic peak (emission wavelength of 414 nm) which could interfere with sample analysis. Cotton blank reference spectra were then used for background comparisons. Also, some cotton products were excluded from use as they were found to contain traces of optical brighteners likely from the inclusion of recycled, formerly brightened cotton.

Laboratory trials with syringe filter capsules (Gelman Science: trademark "Acrodisc" and "Acrodisc PF"), in which 0.2 um-pore polyethersulfone membrane filters preferentially sorbed optical brighteners (Fay, et al, this publication) during column experiments, was followed by field sampling utilizing disposable syringe and peristaltic and manual vacuum pump collection methods. Insufficient data precludes reporting at this time.

Solid phase fluorometry was performed at the University of Minnesota Hydrogeochemistry Laboratory utilizing a Shimadzu RF5000U scanning spectrofluorophotometer, lab-developed methodologies and electronic data storage and processing (Fay, et al, this publication). Pure optical brighteners were obtained from Ciba-Geigy (1989) [Trademark: Tinopal CBS-X (ASTM DSBP-1) and Tinopal 5BM-GX (ASTM DASC-4)] to provide reference spectra for the two most common optical brightener derivative groups. Because of the proprietary nature of laundry product formulations, popular liquid and solid detergents were purchased, fluorometrically analyzed and compared with the pure optical brightener reference spectra. Excitation, emission and synchronous scans of calibrants, blanks and samples were conducted, and 60 nm synchronous scans were utilized to match 440 nm reference and sample peaks yielding positive FWA detections above the background cotton blank spectra. Several to many scans were run of each sample to ensure surface area coverage, and indeterminate results were treated as negatives.

***Water Supply Sampling and Analysis***

Sites were sampled periodically from taps supplying cold, untreated water close to the well. Water was allowed to run for 45 or more minutes until stabilized, i.e., 1 percent or less variation of temperature, pH, oxidation-reduction potential, specific conductance and dissolved oxygen. Stabilization instruments (YSI, Inc.: Model 3560 Water Quality Monitoring System and Model 50B Dissolved Oxygen Meter) were calibrated before each sampling event and then cleaned and rinsed with distilled water thereafter. Sample taps were flamed with a propane torch, and then water was allowed to run an additional 5 minutes before sampling. Appropriate sample containers, preservatives and coolers were utilized in accordance with Standard Methods (APHA, AWWA, WEF, 1992), as were the analytical protocols for the examination of the water samples whether in the field [e.g., total and bicarbonate alkalinity (titration) and ammonia/ammonium-nitrogen (Orion Model 290A ion selective electrode meter)], at contracted Minnesota Department of Health-certified environmental laboratories or the University of Minnesota Hydrogeochemistry Laboratory. A field and laboratory quality assurance plan was followed to ensure the representivity, precision and accuracy of the test results.

## RESULTS AND DISCUSSION

Thirty-five sites were selected among the four communities with the majority sampled periodically over the 1993-1995 project period. Table 2 summarizes fluorometric, physicochemical and bacteriological data collected with mean, range or percent positive reported for selected analytes.

Table 2. Water Supply Test Data and Optical Brightener Detections from Four Communities

| Parameter | Castle Rock | Coates | Empire City | Vasa |
|---|---|---|---|---|
| Sample Sites | 7 | 9 | 4 | 4 |
| Positive FWA's | 29% | 89% | 50% | 75% |
| pH (units) | 7.06 [6.75 ~ 7.33] | 7.13 [6.48 ~ 7.65] | 7.15 [6.66 ~ 7.42] | 7.05 [6.33 ~ 7.32] |
| Redox Potential (mV) | +146 [-56 ~ +212] | +146 [+123 ~ +166] | +140 [+111 ~ +173] | +132 [+117 ~ +149] |
| Conductivity (mS/m) | 82.8 [71.3 ~ 108.3] | 83.3 [59.8 ~ 120.1] | 60.9 [41.1 ~ 69.7] | 84.3 [69.0 ~ 119.8] |
| Tot Dis Solids (mg/L) | 509 [446 ~ 650] | 513 [383 ~ 715] | 389 [280 ~ 437] | 518 [433 ~ 713] |
| T Hard (mg CaCO3/L) | 386 [346 ~ 475] | 388 [305 ~ 516] | 309 [240 ~ 340] | 391 [338 ~ 515] |
| Tot Coli Bacteria-pos | 22% | 18% | 14% | 25% |
| Nitrate-N (mg N/L) | 7.9 [<0.2 ~ 15.5] | 11.8 [6.8 ~ 20.4] | 8.5 [0.2 ~ 12.2] | 8.2 [0.6 ~ 13.0] |
| Chloride (mg/L) | 64 [26.7 ~ 131] | 67 [14.2 ~ 110] | 18.6 [15.8 ~ 26.6] | 65 [36 ~ 111] |
| Sulfate (mg/L) | 45 [24.7 ~ 62] | 30.5 [28.0 ~ 33.1] | 24.2 [22.7 ~ 25.6] | 37 [24.0 ~ 55] |
| Tot Alk(mg CaCO3/L) | 259 [221 ~ 340] | 262 [205 ~ 355] | 220 [195 ~ 255] | 260 [225 ~ 375] |

*NB: One or more samples/site; mean [minimum~maximum]; percent positive; T / Tot = total; mV = millivolts; mS/m = millisiemens/meter = 10 umhos/cm; mV = millivolts; mg/L = milligrams/liter; N = nitrogen; CaCO3 = calcium carbonate*

Immersion filter holder media, depending upon length of exposure, water quality and other factors, were prone to physical erosion (surficial cotton fibers), masking by precipitates (e.g., carbonate scaling, iron hydroxides and staple corrosion), bacterial colonization (e.g., iron bacteria) and adsorption site competition. At spring sites, the physical removal of cotton fibers was aided and abetted by colonized bacteria and their consumption by grazing aquatic invertebrates. Despite cotton's sorptive affinity for optical brighteners, negative or indeterminate fluorometric results were sometimes reported when one or more of the above conditions occurred.

***Castle Rock***

Castle Rock was selected because of available water quality data and continuing investigations of significant groundwater impacts from former herbicide spill and rinsate disposals (Minnesota Superfund Site), residential and commercial waste dumping and road salt stockpiling, as well as the presence of nonconforming and failed septic systems (cesspools, seepage pits and nonconforming drainfields). Originally, 18 sites were chosen, but a County-sponsored well replacement project during 1993-94 removed 11 sites from this study. Before 10 of the 11 existing wells were disconnected and sealed, abbreviated screening tests were conducted with negative results for optical brighteners.

However, one well (site 1009) disconnection was delayed several months allowing additional exposure time and strong positive optical brightener results (Figure 2). These results are compared with site 1033 which has been consistently negative. Because the owner of site 1009 had plumbed the toilet with hot water to prevent condensation during the summer months, we surmise that cotton sorption of optical brighteners was enhanced by increased water temperatures. Optimum FWA adsorption varies with its solubility in water, temperatures between 15 and 50 degrees Celsius and other factors (Ciba-Geigy, 1989). Since ambient groundwater temperatures are colder (7 to 12 degrees Celsius), the obvious answer was to prolong the filter holder exposure time. Unfortunately, increasing the period of immersion to facilitate slower FWA adsorption likewise increases the masking of the cotton by precipitates and bacterial colonization which reduces the available surface area for FWA adsorption.

Completing the sampling and analysis of the remaining sites may provide additional clues to FWA detection problems in moderate ionic strength groundwater environments with mixed-source contaminants.

***Coates***

The City of Coates was chosen for its thick unsaturated zone of outwash sand and gravel overlying weathered dolostone, its proximity to large agricultural tracts and the Rosemount Research Center (National and Minnesota Superfund Site), and the prevalence of nonconforming septic systems (cesspools, seepage pits and deep, undersized drainfields). Rapid recharge and oxidation accounts for the consistently elevated nitrate, total dissolved solids, chloride and some fecal bacteria breakthrough (Table 2.). These correlated well with the 89% positive optical brightener detection rate although earlier samples at the same sites were less likely to be positive. As with Castle Rock, the early Coates negative results probably represent the early stage of the study when methods and materials were being refined, as well as possible dilution of optical brighteners during heavier precipitation periods.

Figure 3 compares an early low positive optical brightener detection from site 1034 [positive coliform bacteria and elevated nitrate (7.6 mg N/L)] with indeterminate results from site 1031 [negative coliform but very high nitrate (20.0 mg N/L)]. Subsequent sampling has given consistent positive results for site 1034 along with repeated positive coliform bacteria. There has been a single positive FWA result for site 1031 but continuing negative results for site 1030 which is adjacent and cross-gradient to site 1031, has a shallower well but similar nitrate, TDS, chloride and other water test results.

Figure 2. Fluorometric Scans - Castle Rock

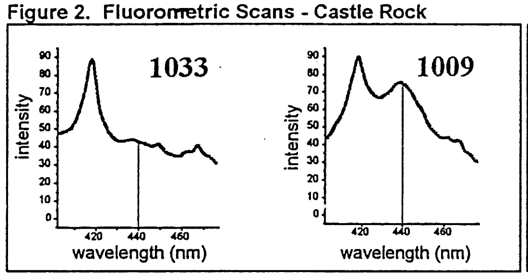
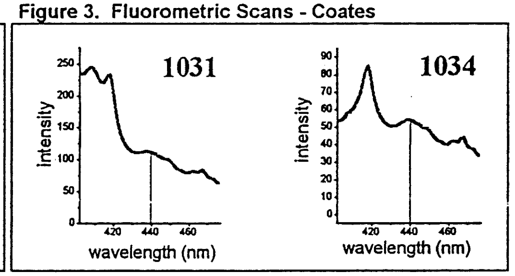



Figure 3. Fluorometric Scans - Coates




***Empire City***

Situated in an alluviated and outwash-filled buried bedrock valley and on and adjacent to the floodplain of the Vermillion River, the village of Empire City is characterized by a very shallow water table in highly permeable sand which has invited drivepoint well installations in basements in close proximity to septic systems (older, nonconforming drainfields and seepage pits are common) and other waste disposal.

Figure 4 contrasts a downgradient well location (site 1035) having a positive detection for optical brighteners on cotton at 440 nm with an upgradient well (site 1028) which yielded indeterminate results. The downgradient well water persists with positive FWA detects but slightly lower nitrate values (9.6-11.0 mg N/L) while the upgradient well is now positive for optical brighteners with nitrate at 11.8 to 12.2 mg N/L. All coliform bacteria tests have been negative.

However, in contrast, a reportedly shallower drivepoint at site 1038 located even farther downgradient than site 1035 has been consistently negative for optical brighteners and coliform bacteria. Nitrate has been 0.2 mg N/L, but most of the other parameters are similar to the water quality of the more upgradient wellpoints. The site is within the floodplain and that may hold the answer to the differences cited.

***Vasa***

An unincorporated village in Goodhue County, Vasa occupies a loess and till-capped upland ridge underlain by weathered sandstone and dolostone, both of which crop out in the vicinity. It appears that locally the fractured and karsted dolostone provides sufficient groundwater for the shallow wells completed in it but is also prone to pollution from waste and wastewater disposal practices. Several residents still utilize both rainwater and groundwater cisterns, but their proximity to deep, nonconforming septic systems and possible interconnection with well-supplied household water are problematic. It appears that all of the older, functioning wells are completed in bedrock with some of the shallower dug wells, now dry, having been converted to sewage pits.

As with the above examples, Figure 5 compares site 4040, formerly with indeterminate optical brightener results, to site 1041 located to its east and slightly downgradient which has had consistently positive detections. Both sites are routinely positive for FWA's now. Another positive FWA site (1045) is northwest and situated slightly downgradient from site 1040. Originally a shallower well, it was "deepened" a number of years ago to a reported 250 feet. However, its water quality is similar to that of the shallower bedrock wells.

Figure 4. Fluorometric Scans - Empire City

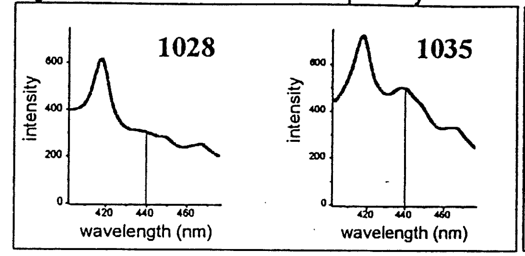
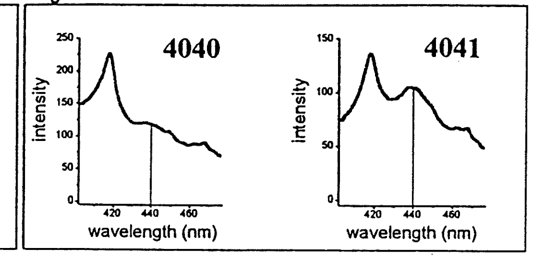



Figure 5. Fluorometric Scans - Vasa




## CONCLUSIONS

Employing novel methods for immersion and in-line sampling of cotton and other selective filter media and solid-phase, scanning spectrofluorophotometric techniques and computer-processed spectral analysis, the development of cost-effective qualitative screening and possible semi-quantitaive testing of optical brighteners (fluorescent whitening agents or FWA's) in groundwaters has been demonstrated in the field and laboratory. The methods obviate the concerns of fluorescent dissolved organic carbon compound interference that hampers low fluorometric detection limits for aqueous samples. Instead, they rely on solid media which preferentially sorbs and accumulates FWA's. By electronically storing excitation, emission and synchronous scans of sample spectra, comparing the results to optical brightener reference spectra at 440 nm, and resolving cotton or other filter media blank interference, relatively low detection limits are feasible. Preliminary correlations with sample site groundwater test data and sanitary survey information on water supply and waste/wastewater practices suggest moderately good agreement in utilizing positive optical brightener detections as indicators of septic system contamination of shallow, unconfined aquifers. The study will be completed with additional sampling and analysis to verify the optical brightener detection system and statistically correlate the data and information. The methods and materials are readily transferrable to surface water and wastewater optical brightener screening and testing.

## ACKNOWLEDGEMENTS

Funding for this research project was approved by the Minnesota Legislature [ML 1993, Chap. 172, Art. 1, Sec. 14, Subd. 11 (i)] as recommended by the Legislative Commission on Minnesota Resources from the Minnesota Environment and Natural Resources Trust Fund. The senior author gratefully acknowledges the assistance of the Dakota County Physical Development Division and Environmental Management Department staff.

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Date of Report: July 1, 1995 *[Revised 1996]*

DEC 13 1996

LCMR Final Report - Summary - Research

I. Project Title: W oth-2 OPTICAL BRIGHTENERS: INDICATORS OF SEWAGE CONTAMINATION OF GROUNDWATERS


Program Manager: Ronald C. Spong, Environmental Program Manager
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A. Legal Citation: M.L. 93 Chpt. 172, Art. 1, Sect. 14, Subd. 11 (i)

Total Biennial LCMR Budget: $157,000

Balance: $22,904.69 *[Unspent residual]*

Liquidated: $134,095.31 *[Amount-to-be-paid to Dakota County: $43,423.64]*

Appropriation Language as drafted 7/27/92: This appropriation is from the future resources fund to the commissioner of the pollution control agency for a contract with Dakota County to study the correlation of optical brighteners present in domestic sewage from detergent use with non-agricultural nitrogen as interferences with atrazine detection.

B. LMIC Compatible Data Language: During the biennium ending June 30, 1995, the data collected by the projects funded under this section that have common value for natural resource planning and management must conform to information architecture as defined in guidelines and standards adopted by the information policy office. Data review committees may be established to develop or comment on plans for data integration and distribution and shall submit semiannual status reports to the legislative commission on Minnesota resources on their findings. In addition, the data must be provided to and integrated with the Minnesota land management information center's geographic data bases with the integration costs borne by the activity receiving funding under this section.

C. Status of Match Requirement: Not applicable.

II. Project Summary


The overall objective is to determine if optical brighteners, organic blue dyes added to detergents to enhance the apparent cleanliness of clothing and, consequently, a component of domestic sewage, can be correlated with other wastewater contaminants, such as nitrates, in groundwaters.





Tests of drinking water supplies derived from several karst groundwater aquifers in southeastern Minnesota have detected low levels of optical brightener fluorescence, as well as indicators and contaminants of domestic sewage origin. By extending the testing to wells in other shallow and intermediate depth aquifers throughout a nine-county area, it is hypothesized that optical brightener levels may cost-effectively predict the on-site sewage system contribution to the deterioration of drinking water quality as compared with agricultural sources with the same contaminants but no such dye use.

An inexpensive detector placed in toilet tank reservoirs to adsorb optical brighteners present in water supplies will be evaluated to determine if it can reliably screen for the qualitative presence of domestic sewage contaminants. Also, possible triazine herbicide residue test interference by optical brighteners may account for some false positive tests in areas of pesticide contamination and other areas with no reported triazine use and will be investigated.


III. Statement of Objectives

A. Conduct optical brightener monitoring program.

B. Evaluate monitoring data and information.

IV. Research Objectives

A. Title of Objective: Conduct optical brightener monitoring program.

A.1. Activity: Conduct field investigations, testing and sampling.

A.1.a. Context within the project: The comprehensive monitoring program for optical brighteners relies upon extensive field work to acquire sufficient data and information from a representative sample of individual well water supplies throughout southeastern Minnesota. A number of different unconsolidated and consolidated formation aquifers of shallow to intermediate depth will be monitored to determine their susceptibility to contamination by optical brighteners, domestic sewage indicators and parameters from other pollution sources including agricultural pesticides.

A.1.b. Methods: The study areas will be selected in nine southeastern Minnesota counties (Dakota, Dodge, Fillmore, Goodhue, Houston, Mower, Olmsted, Wabasha and Winona) to represent a number of shallow and intermediate depth groundwater aquifers with different unsaturated and saturated zone thicknesses and compositions. The study areas will include a range of population densities, land uses and perceived or known problems, as well as different types of well construction and drinking water supply systems.

Environmental specialists and technicians will be trained to conduct sanitary surveys of selected individual well water supplies, sewage systems and building occupancies which include:

1. Well construction, protection, abandonment, sealing;
2. Water supply system components (plumbing, storage, treatment);
3. Cross-connection control, backflow/backsiphonage protection;

4. Pollution sources (sewage system, dry well, fuel tank, etc.);
5. Water consumption, use, previous test results, problems;
6. Detergent use and disposal (other optical brightener sources);
7. Consumer health/acceptance, anecdotal information on illness;
8. Field testing and measurements; and
9. Representative sampling for laboratory analysis.

A questionnaire will be developed addressing pertinent elements of the above survey items and will be administered to study participants by trained personnel. In particular, the questionnaire will request information on both current and historical water usage, waste disposal, detergent selection, laundry regimen and other events, behaviors and choices that may be related either directly or indirectly. Anecdotal information will also be recorded to verify observations and permit working hypothesis modifications.

In most cases, the sanitary surveys of individual water supplies will be completed during sampling and field testing to ensure the control of those attributes which may otherwise bias or confound the study results or their interpretation. These include dual water supplies, cross connections, backflow and backsiphonage, recent or continuous disinfection, water treatment devices and unused, abandoned wells.

Particular attention will be focused on the components of the wastewater system to determine if two or more systems exist. For example, an upper story drainfield treatment area and a separate basement dry well disposal would indicate that laundry wastewater may be more directly entering the domestic water supply because of the proximity of the well to the disposal source. Also, other types of waste disposal will be investigated (dumps, etc.) where optical brighteners could possibly be released in addition to building sewage.

Field testing will be accomplished at each site to ensure the representative sampling of groundwater for laboratory analysis. This will include stabilization tests for temperature, specific conductance, pH and oxidation-reduction potential utilizing a YSI 3560 Water Quality Monitor. Field, as well as laboratory, testing may be conducted for certain parameters utilizing a Hach DR/EL-2 Environmental Laboratory if subject to change due to destabilizing conditions.

Field fluorometric analyses may be performed at certain sites to determine background fluorescence, identify possible interferences and verify problems and assumptions. Grab samples will be collected, preserved, stored and handled in accordance with approved U.S. EPA (Environmental Protection Agency) METHODS and STANDARD METHODS whether analyzed by study or contract laboratory personnel. Chain-of-custody procedures will be followed to ensure sample data integrity and compliance with the study's quality assurance plan. Duplicate samples will be collected at random, and trip and field blanks will be utilized for certain parameters which are subject to contamination, interference, volatilization or other problems.

Sites selected for resampling may have the reservoirs of high-use toilets cleaned and chlorinated to allow for the installation of unbleached, undyed cotton detectors for long-term monitoring of optical brighteners. Qualitative adsorption of dye by the



detector over time will be compared with the quantitative results, as well as other parameters of contamination. Verification of this qualitative screening method may also be tested by installing detectors at sites both before and after groundwater sampling and field analysis. Experimentation with different screening methods will be conducted concomitantly to assess selectivity, sensitivity, cost and other factors.

Also, sites will be carefully evaluated with respect to soil and bedrock geology and hydrology, topographic characteristics, surface water drainage and wetlands, land-use history and other information pertinent to the study. Possible movement of wastewater in the unsaturated zone will be reviewed to determine the likelihood of migration to groundwater discharge points different than the source location. Verification may be made in some cases by utilizing other tracers or increasing the number of sites sampled to include adjacent and downgradient water supplies.

A.1.c. Materials: Field materials necessary to accomplish this objective include vehicles, topographic maps, soil surveys, surveying instruments, soil coring tools, water sampling stabilization instruments, portable environmental laboratories, sample containers and coolers, portable fluorometers and equipment, unbleached cotton detectors, chlorine bleach, distilled water, field notebooks, calculators and survey, test and sampling forms.

A.1.d. Budget: $57,000
Balance: $ 0

| A.1.e. Timeline: | 7/93 | 1/94 | 6/94 | 1/95 | 6/95 |
|---|---|---|---|---|---|
| Design program | ********** | | | | |
| Conduct field work | | ********************************************** | | | |

A.2. Activity: Conduct laboratory analysis and quality assurance.

A.2.a. Context within the project: The laboratory analysis of samples of individual water supplies collected during the field investigations will form the majority of the data on optical brighteners, pollution indicators, contaminants and background parameters required for the evaluation phase of the study.

A.2.b. Methods: Analyses will be divided between a project fluorometry and physicochemistry laboratory and one or more more contract environmental laboratories. Laboratories utilized for the analysis of Safe Drinking Water Act parameters will be currently registered or otherwise approved by the Minnesota Department of Health Division of Public Health Laboratories.

Approved analytical methods will be utilized for all required bacteriological and physicochemical parameters in accordance with the current editions of STANDARD METHODS, EPA METHODS or other accepted consensus standards. Additionally, laboratories will have a quality assurance/quality control program which will be reviewed periodically to ensure that data generated by the study meets accepted standards and practices.

The fluorometry laboratory will be established to expeditiously handle photosensitive samples and optimize fluorometric techniques in the analysis of optical brighteners.

Controls will include reference samples of optical brightener dyes and detergent formulations containing such dyes. Other filters and lamps will be utilized to evaluate other fluorescent chemical species that may interfere with optical brightener detection. A scanning spectrofluorophotometer will be sought to facilitate such work, as well as to possibly aid in the separation and identification of similar fluorescent blue dyes.

The bacteriological and physicochemical parameters to be analyzed for a majority of the samples collected include: laboratory pH, laboratory temperature, laboratory specific conductance, total dissolved solids, total and calcium hardness, total and bicarbonate alkalinity, chloride, sulfate, nitrate, nitrite, ammonia, Kjeldahl nitrogen, orthophosphate, total phosphate, silica, sodium, potassium, iron, manganese, total and fecal coliform bacteria, fecal streptococcal bacteria and heterotrophic bacteria (standard plate count). In addition, some selected samples will be analyzed for metals (e.g., lead, copper and chromium), triazine herbicides and volatile organic compounds related to study objectives.

Minnesota Department of Health and Minnesota Department of Agriculture-approved methods for the analysis of triazine herbicide residues will be evaluated with respect to the determination of possible false positives. Reference samples of commercial triazine products will be utilized where appropriate and obtainable, as well as optical brighteners, to test the hypothesis that under some conditions optical brighteners may mask, interfere with or be mistaken for atrazine or other triazine herbicides.

Unbleached cotton detectors will be evaluated qualitatively by developing desorption techniques and fluorometrically scanning for excitation and emission wavelengths. Although it is not likely to be directly quantitative, a variety of techniques may be evaluated to determine if the results can be quantifiable should the volumetric flow be known.

A.2.c. Materials: Laboratory materials required to meet this objective include a fluorometer and appurtenant equipment and supplies, wet chemistry instruments and supplies, refrigerator/freezer, reference samples, reagents, distilled water and data forms. Specific contracts with approved environmental laboratories will be required.

A.2.d. Budget: $75,000
Balance: $12,500

| A.2.e. Timeline: | 7/93 | 1/94 | 6/94 | 1/95 | 6/95 |
|---|---|---|---|---|---|
| Set up fluorometry lab | *************** | | | | |
| Contract labs selected | ************ | | | | |
| Conduct sample analyses | | ************************************************** | | | |
| Review quality assurance | | *** | *** | *** | *** |

A.3. Status:

A.3.a. Problems:

The Dakota County Board of Commissioners approved a contract on July 27, 1993, for project cost reimbursement with the Minnesota Pollution Control Agency, and



all signatories to the document completed their approvals by September 30, 1993. However, the project did not begin immediately because of a number of problems.

Delays in full project start-up were administrative, contractural and logistical and persisted until March 1994 when the program manager was assigned nearly full-time for the remaining 16 months. A reallocation of his supervisory duties to a senior staff member was necessary to continue ongoing environmental management programs. The full-time temporary position that had been budgeted to provide the project's technical field support was eliminated. In retrospect, the latter position would have allowed more efficient use of the program manager's time.

With the exception of contract and purchased services, all program activities were accomplished by the program manager. During the biennium, the program manager worked 4143 hours on the project with 2740 hours supported by State funds and 1403 hours unpaid. During the biennium, the program manager was to have been assigned 80 percent time to the project (3341 hours) [the county contributing 25 percent or 835 hours and the State funding 75 percent or 2506 hours of his salary and fringe benefits]. After the biennium, Dakota County supported 175 hours of the program manager's continuing work on the project. Concomitantly, the program manager worked 740 hours unpaid during 1995-96 on project-related data analysis, presentations, and additional research.

In the fall of 1993, the program manager completed setting up his Turner 111 fluorometer for field and laboratory analysis of samples to detect optical brighteners and other dyes. As preliminary development of the fluorometric detection system continued, it became apparent that ambient groundwater concentrations of optical brighteners in the areas evaluated were very low, probably due, in part, to several years of above normal precipitation. Also, naturally occurring dissolved organic carbon compounds having fluorescent properties in the range of 300 to 500 nanometers (nm) interfered significantly with low level optical brightener detection.

In consultation with Professor E. Calvin Alexander of the University of Minnesota Geology and Geophysics Department, the utilization of the Hydrogeochemistry Laboratory's recently acquired Shimadzu RF5000U scanning spectrofluorophotometer was requested. Capable of computer-processed, simultaneous excitation, emission and synchronous scans of aqueous, elutant and solid phase samples, the instrument could possibly provide very low optical brightener detection limits and help resolve the problem with interfering fluorescent dissolved organic carbon compounds (FDOC's).

A contract with the University of Minnesota was approved on February 2, 1994, by the Dakota County Board of Commissioners. The contract amount of $32,519 included scanning spectrofluorophotometry and the services of a graduate student, Steffan Fay, and a Junior Scientist, Scott Alexander. The contract also resolved the problem of a separate purchase of a spectrofluorophotometer (cost: $30,000). The instrument and laboratory had been used for groundwater dye tracing, but it was necessary to establish field and laboratory protocols, procedures, et cetera, for "part per trillion" range detections of optical brighteners in ambient groundwaters. As it turned out, the latter was no small feat as optical brighteners are ubiquitous. They easily contaminate samples and other materials if scrupulous safeguards are not followed in the field and laboratory. For example, lint from clothing was a nemesis.

The key to the project's success was the public's acceptance and participation. Overall, an average of 20 percent of the building occupants contacted by the program manager agreed to allow access to their premises to install and retrieve filter holders, sample water supplies and inspect utility (wells and water supply lines, waste and wastewater disposal and treatment, etc.) construction and operation.

There were many problems with public, door-to-door queries in rural areas, including the following examples:

1. The program manager's Dakota County picture identification card created some confusion and perhaps resistance south of the Cannon River, and a generic LCMR or Minnesota identification card may have met with greater acceptance.
2. A brochure was prepared, distributed and modified but was ineffective compared with door-to-door salesmanship in securing potential participants. The personal approach, while more time consuming as it meant prolonged contact or repeated visits to speak with spouses, etc., was decidedly more successful.
3. The offer of free water supply testing was often greeted with skepticism and even suspicion. Potential participants would only consider such testing if the results were confidential with limited access by others, especially local and state health and environmental agencies. In fact, it was the program manager's affiliation with the latter agencies that terminated many queries because of public paranoia concerning the condemnation of contaminated wells, failed sewage systems and other waste disposal devices which were the subjects of investigation.
4. Often both spouses or both renters and owners needed to hear the details and approve of them otherwise the return site visit would be unwelcome and/or would find the filter holder discarded. In particular, permission from the male half of an occupancy proved to be critical confirming that rural life is still male-dominated.
5. Lifestyles, including both spouses working and other out-of-home activities, made it difficult to schedule access for sampling and required the program manager to work weekday early mornings and evenings, weekends and holidays. Frequent, missed appointments were particularly time consuming and resource wasting because of the large project area.
6. Complete access to buildings and property was denied in many cases with the owners' veracity offered in place of the program manager's inspections. This invariably led to unverifiable assumptions that the program manager was hoping to avoid by comprehensive sanitary surveys.
7. Over the course of the project, property transactions, divorces, deaths and major illnesses significantly altered some site accessibility, as well as benevolent relationships with participants.

The task of inspecting and sampling 200 sites scattered throughout the nine-county southeastern Minnesota area was demanding as originally planned but should have been revised when the technical support position was eliminated, project startup was delayed, and problems with sampling media and fluorometric analysis were found. Consequently, during the late spring and summer of 1994, the program manager curtailed most new site acquisition and focused on nearby sites to conserve time, mileage, and expenses, as well as to focus on accessible, established sites.

By the late fall of 1994 and winter of 1995 when most of the problems were being resolved and new discoveries were being made, there was insufficient time to reasonably acquire a total of 200 sites. A conscious decision was made to focus on the already selected communities being studied by enrolling additional sites and resampling. Subsequently, only 109 of the planned 200 sites were enrolled.



The decision was also made to exclude the approximately 30 randomly selected sites when continuing problems with participant enrollment emerged. Additionally, cultural changes not reflected on outdated topographic maps (20 to 30 years old), as well as other dated information utilized for randomization, proved to be formidable.

Although the project became more limited in scope with respect to number of sites and communities, the program manager attempted to offset that impact by ensuring the variety of variables represented and thus rigorously test the working hypotheses. Early project work focused on prospecting the southeastern Minnesota area for uniquely different communities in a variety of cultural, topographic, hydrogeologic, and other environmentally variable settings, and 37 potential candidate areas were found from which 21 communities were selected (Table 1.). The remaining communities and potential participants are available for continued study should funds be made available.

To improve acceptance by potential participants, it was necessary to modify and simplify the questionnaire and the sanitary survey. Instead of working from and filling out forms, questions were verbalized to personalize the interaction with potential participants and improve the chances of enrolling sites. The informal and personal approach proved to be successful for soliciting participation. Replies to leading questions prompted more specific questions. The program manager carefully explained pertinent facts and recommendations to address concerns inevitably raised by participants. Obviously, the public's need to know and understand environmental health and safety facts and issues is very significant but is largely unmet. An environmental folklore has developed in its place which perpetuates unreasonable fears, promotes doubtful or bogus remedies, and reinforces harmful habits and practices. The need for environmental health education is paramount considering the direct and indirect benefits of prevention.

Often, potential participants were loathe to allow complete access to their premises for the program manager's inspection of the well, water supply and wastewater systems, especially if it meant entering a basement or less frequented area. This compromise was allowed whenever required to ensure enrollment. Accepting participants' statements in lieu of more technical observations may have led to assumptions on the part of the program manager that may not necessarily have been represented by fact. Follow-up site visits were made to address certain facts that may still have been in doubt, but a number of sites still could not be inspected thoroughly.

Laundry product usage became moot early in the project when it was determined that almost all detergents and other laundry products contain mixtures of both chlorine bleach-resistant and non-bleach-resistant optical brighteners (0.1 to 2 percent by weight) regardless of "dye-free" assertions on the packaging. Rather, the appropriate questions regarded whether any laundry cleaning was done on the premises and where the wastewater was discharged (sewage treatment system, seepage pit, dry well or surface ditch).

Toilet tank reservoirs continued to be the location-of-choice for immersion filter holders containing cotton and other filter media. The tanks protected the filter holders from disturbances and light (photodecay of optical brighteners is significant). However, the cleaning and disinfection of toilet tank reservoirs was not performed because of the prevalence of chlorine bleach-resistant optical brighteners and the decision to maintain the status quo practices of building occupants and, therefore, minimize the introduction of new and unknown variables. Observations over the project period revealed that many tanks were colonized by bacteria (primarily iron oxidizing and sulfur reducing species) and molds which spread by the airborne drift of capsules and spores. The longer the period of filter holder immersion was, the more likely that some filter media would support bacterial growth (cotton and activated carbon but not polysulfone/polyethersulfone filter membranes) which contributed to the masking of adsorbent surfaces and diminution of optical brightener adsorbence.

Immersion filter holder design, fabrication, filter media contents and placement evolved over time with the recovery of older, exposed immersion filter holders (IFH). Although the IFH concept has been used by other workers in the field of fluorescent dye tracing, the aspect of long-term placement for the potential adsoption of ambient, very low concentrations of various fluorescent dyes rather than larger injected dye quantities was untested. The following details the problems that occurred and the resolutions that were developed:

1. Black, very fine-mesh window screening was selected because steel screening corroded, aluminum screening lacked strength and was costly, and cellulose milk socks (used for immersion holders for fluorescent dye tracing) contained optical brighteners.
2. Depending upon the type and amount of filter media contained, the IFH varied from large (approximately 4 inches by 6 inches) to small (3 inches by 4 inches or 3 inches square). They were folded twice for strength and gross filtration from a larger, rectangular sheet of triple-rinsed (deionized distilled water) Fiberglas window screening.
3. Stapling proved to be the best method for fastening the screening together even though individual staples rusted and occasionally opened. Increasing the number of staples resolved the problem.
4. The means of IFH attachment to the toilet tank's standpipe was resolved using plastic tywrap of various lengths although it proved less flexible. White and translucent tywrap was not utilized as it tested positive for optical brighteners.
5. In spring ponds and runs, several different problems occurred as described as follows:
    - a. Variable discharge rates subjected IFH's to substantial movement, physical abrasion and erosion of the contents. Monofilament fishing line worked well in securing IFH's to above water surface reference points.
    - b. Cotton pads were severely eroded, and frequently little or nothing remained after variable exposure periods because of the following:
        - i. Physical loosening and removal of the cotton fibers by turbulent flow, suspended and streambed materials and pounding against rocks.
        - ii. Bacterial and fungal colonization of the cotton fibers as an organic substrate and nutritive source.
        - iii. Consumption of cotton fibers or grazing of their surface by macroinvertebrates (e.g., sideswimmers).
    - c. Masking of IFH or contents by detritus, precipitates and sediment.

Another aspect of optical brightener sorption that was recognized but difficult to overcome is the effect of temperature on adsorption rate. While laboratory trials were conducted at sample temperatures of 20 to 25 degrees Celcius, average groundwater temperatures of 10 degrees Celcius in southeastern Minnesota appear



to slow adsorption rates consequently requiring extended exposure time to achieve similar results thereby increasing the likelihood of masking. Anecdotedly, two sites (1009 and 1081) had hot water plumbed to the toilets to prevent condensation drips, and optical brightener sorption appears to have been significantly enhanced. Also, reference samples of optical brighteners have a wide range of adsorption temperatures (15 to 50 degrees Celcius), all of which are warmer than the groundwaters sampled.

The serendipitous discovery* that polyethersulfone (PES) and polysulfone (PS) membrane filters preferentially sorb optical brighteners offered both important research directions and an overextension of limited resources. While the decision to explore the filter media proved successful, it also delayed or diminished other aspects of the project. [*The use of PES membrane filters was accidental for collateral sand column experiments. A solution containing four water tracing dyes, including optical brighteners, was prefiltered. Nearly all of the optical brighteners were found to have been retained by the prefilter since almost no optical brighteners were detected after passing through the sand column.]

Originally, contracts with registered environmental laboratories were considered. Because the project spanned a biennium and it was unknown which of the reviewed laboratories would be selected, it was determined that more informal, negotiated prices for purchased services would allow flexibility should laboratory performance or costs become issues. As it turned out, this was a good choice and allowed continued bargaining to secure reasonable prices for the laboratory work. The majority of the environmental laboratory work was performed by the Olmsted County Health Department's Environmental Laboratory in Rochester and the Minnesota Valley Testing Laboratories in New Ulm.

Additionally, water sample geochemistry was split between field analyses by the program manager (those parameters subject to immediate, significant changes) and more sophisticated instrumental analyses by the University of Minnesota's Hydrogeochemistry Laboratory. A hidden benefit to this approach was the analysis of the same parameter by different laboratories and, in some cases, different methodologies, which enhanced quality assurance tracking. (Tables 2. & 3.)

The objective to ascertain if optical brighteners interfere with the detection of chemically related triazine herbicides, specifically atrazine, by causing false positive results when atrazine is actually below method detection limits, is inconclusive based on the limited testing performed. Aatrex 9-0 (trademark), dry, flowable atrazine product of Ciba-Geigy (85.5 percent pure atrazine, 4.5 percent atrazine derivatives and 10.0 percent inert ingredients), was obtained and is the same or similar to atrazine products currently in use. Experiments utilized approved methods for atrazine analysis, and both field samples and laboratory-prepared samples with and without standard additions were utilized. It appears that current approved assay methods for atrazine residues discriminate between true atrazine concentrations and known additions of optical brighteners.

A.3.b. Progress:

A fluorometric detection system has been designed and tested for optical brighteners (also known as fabric whitening agents or FWA's) which are synthetic organic blue dyes that fluoresce bluish-white upon exposure to ultraviolet light and that are utilized in laundry products and consequently discharged with domestic wastewater to sewage treatment systems. The detection system is comprised of several types of filter holders with adsorbent, selective media, a solid and liquid phase scanning spectrofluorophotometer and computer software-driven data manipulation for comprehensive and objective analysis. The system has been used successfully in detecting treated effluent from municipal wastewater treatment facilities (WWTF) and their downstream receiving waters, treated and untreated on-site sewage treatment system effluent and treatment area infiltration and percolation to groundwater, surface streams and groundwaters. (Attachment 1.)

The detectors included immersion, in-line and syringe filter holders which contained a variety of adsorbent filter media (untreated cotton pads, activated carbon and polysulfone/polyethersulfone membrane filters) which were exposed to long-term immersion, short-term in-line and short-term syringe flows. The immersion filter holders were placed in the tank reservoirs of the most used toilets in residences and businesses, spring ponds and runs, treated municipal WWTF effluent outfalls, on-site sewage treatment system effluents and surface streams. In-line filters were attached to untreated, cold water taps for continuous sampling, and syringe filters with polyethersulfone membranes were used to discretely sample drinking water, treated wastewater effluent and surface streams.

The untreated cotton was selective for optical brighteners provided blank pads were scanned for trace optical brighteners (certain manufacturers utilize recycled cotton which may have been previously brightened) and for native fluorescence of cotton (optimum emission wavelength of 415 nm) which could interfere with low level optical brightener detection (optimum emission wavelength of 440 nm). Concern for fluorescent dissolved organic carbon compound (FDOC) interference (emission wavelengths of 200 to 450 nm) was resolved by utilizing solid phase fluorometry. However, cotton's utility is impacted by the masking of fibers by precipitates, sediment and bacterial colonization and by physical fiber erosion, microbial degradation and other fiber destruction or removal.

Untreated cotton is a conservative and highly selective adsorber of optical brighteners but is limited to qualitative detection methods indicating simply presence or absence of optical brighteners. The optimum exposure period for cotton immersion filter holders appears to be 4 to 12 weeks but is dependent upon a number of variables [water temperature ($\geq$ 15°C), absence of strong oxidizers (e.g., chlorine bleach even though some FWA's are bleach-resistant), insignificant cotton fiber erosion, and minimal masking (precipitates, microbial slime, etc.)].

The likelihood of optical brightener contamination from extraneous sources [e.g., clothing lint, recycled cotton (including supposedly raw surgical cotton), and leaching from optical brightener containing products] is very real and subjects the unwary practitioner to preventable false positive detections. Random blanks were run on raw materials, prepared products, and handling/storage equipment. Every lot of cotton used was checked several times. To avoid lint and other unknown sources of optical brighteners during filter holder assembly, the program manager constructed and used a glove box, similar to those used in sterile laboratories. The completed filter holders were sealed in sterile sample bags while still in the glove box and not removed until the moment of installation at the sampling site. Such precautions were necessary as evidenced by some rejected lots of cotton pads and a filter holder lot.



Optical brighteners may also be detected with semi-quantitative methods utilizing in-line or syringe filter sampling methods and comparing the results with reference sample exposures [Optical Brightener Index (OBI)]. However, the latter semi-quantitative methods require two-point calibration standards and additional testing to ensure reliability and validity. Solid phase spectrofluorophotometry requires repeated manipulation of a sample to accumulate a sufficient number of successive scans from which an average value can be reported. By sandwiching a third cotton pad between two outer exposed pads, the program manager created an internal check for obviously negative OBI values paired with potentially positive values.

Activated carbon was used primarily in the project as a means of monitoring FDOC concentration and the potential of optical brightener interference. However, it has utility in sorbing other fluorescent, organic dyes that may be associated with pollutants. For example, the fluorescent yellow-green dye fluorescein is used as a colorant for the antifreeze, polyethylene glycol, which is toxic and, when improperly disposed after use, may contain dissolved metals, such as lead. Rhodamine is a fluorescent pink dye used to mark, for example, pesticide-treated seed, transmission and hydraulic fluids, and other toxic products.

Soluble, residual dyes may eventually leach to groundwater. However, since they may have many different sources, their detection only indicates that more testing is necessary. Charcoal-adsorbed dyes must first be elutriated from the carbon by a strong base in a water-based solvent system and then the elutant is analyzed spectrofluorophotometrically for dye type and concentration. A complete detection system should include activated carbon, as well as untreated cotton.

Concomitant with and supported by the project's methodologic preparations, the graduate student, Steffan Fay, applied to the National Ground Water Association for a research grant to study the movement and retardation of optical brighteners through a sand column. Awarded a grant of $1000, he ran a mixture of dyes, including optical brighteners, dissolved in pristine, uncontaminated groundwater through a column packed with outwash sands recovering them with continous scanning spectrofluorophotometry. The recoveries of eosin and, in particular, optical brighteners were very poor. A meticulous search for an answer was rewarded in the serendipitous discovery that the prefilter [Gelman Acrodisc PF (trademark)] to the scanning spectrofluorophotometer's flowthrough cuvette was sorbing some of the eosin and most of the optical brighteners. Further study demonstrated that the 25-mm diameter membrane filters, in particular the 0.8 micron pore filter, comprised of polyethersulfone accounted for nearly all of the optical brightener adsorption.

Subsequently, laboratory and field experimentation with polyethersulfone and polysulfone membrane filters [Gelman trademarks: Acrodisc PF, Acrodisc, Supor, Tuffryn, BioTrace and UltraBind] was conducted in two of the three sampling modes, namely immersion and in-line filter holders. The immersion sampling mode for polysulfone/polethersulfone is ineffective probably due to no flow through the membrane filter which would increase the sorbing surface area and mass of optical brighteners available for sorption. The in-line sampling mode received the least number of trials with mixed results and will be continued with very low concentration standard additions of optical brighteners to determine semi-qualitative recoveries of optical brighteners when paired and exposed with and without standard additions. Blanks of membrane filters, triple deionized distilled water and optical brightener standard serial dilutions will be run.

Correlation of positive detections of optical brighteners with the microbiologic and physicochemical attributes of the water supply is mixed depending upon the parameter of interest. Data analysis is continuing, and it appears overall that chloride concentrations above regional background levels (< 5 mg/L) are the most sensitive indicators of sewage contamination of groundwaters considering their correlation with the presence of optical brighteners. However, chloride, by itself, is not a reliable sewage contamination indicator as it has many potential sources [e.g., road salt and water softener wastewater (which is often improperly disposed in surface drainage)]. The low chloride concentrations correlated with problem-proven well water supplies suggest that chloride alone is a poor predictor of contamination unless augmented by a number of other indicators and/or contaminants.

Interestingly, Alhajjar, et al, 1990, in a study of the performance of central Wisconsin on-site sewage treatment systems, monitored shallow drivepoints for the sampling of perched or shallow groundwater near the treatment areas and determined that chloride was the most significant sewage system indicator. However, they dismissed optical brighteners as reliable indicators. But problems with design, sampling and analysis, including the sole use of a non-bleach resistant optical brightener and older filter fluorometric technology, may have hidden the answers.

Correlations with the traditional sanitary indicators, namely total coliform bacteria and nitrate-nitrogen, were not particularly significant. Studies (Bitton and Gerba, 1984) have determined that coliform bacteria are readily strained out by soils and survive poorly outside of their human and animal hosts. Likewise, nitrate is but one form of nitrogen and requires aeration, favorable oxidative chemistry and soil microbiology. Since sewage nitrogen is primarily in the reduced forms of inorganic ammonia and organic nitrogen compounds, the absence of nitrate in a drinking water supply does not necessarily imply it is safe as folklore would have one believe. Certainly, the presence of ammonia or ammonium ions, soluble organic nitrogen and/or nitrite should be cause to examine the water supply more closely as they suggest the presence of a close source of nitrogen contamination (or possibly colonization by denitrifying bacteria).

In communities where a thick unsaturated zone is present with a deep water table aquifer, the study found a stronger correlation between elevated nitrate-nitrogen and optical brighteners. In Coates, nine residences were examined and, when sewage source, well depth, and groundwater flow direction were considered, the correlations became significant and logical.

Therefore, qualitative detections of optical brighteners as either presence or absence (not quantitatively with the present methodological limitations) must be assessed with sanitary and other test parameters and the relative hydrogeologic plausibility for contaminants to be released from a sewage source and migrate to and impact a water supply.

To date, four papers have been presented on the project, and two have been published (Attachments 2 & 3). The graduate student, Steffan Fay, whose work was funded in part by this study, has completed three Plan B papers related to optical brighteners in partial fulfillment of a Master's degree in geology and geophysics from the University of Minnesota. Additionally, the program manager, at his own expense, is assisting Carver County environmental health officials with a study of the Carver Highlands area in which elevated nitrates is a continuing concern. Optical



brighteners and other parameters are being analyzed in an attempt to determine whether on-site sewage system nitrogen or agricultural nitrogen is the primary cause of the problem.

B. Title of Objective: Evaluate monitoring data and information.

B.1. Activity: Organize, review, maintain datafiles, statistically analyze and evaluate data and information collected. Submit draft reports for peer review. Conclude study and submit final report.

B.1.a. Context within the project: During and upon the conclusion of the field and laboratory data acquisition phase of the study, all information and data will be organized, reviewed and, wherever appropriate, entered into datafiles for ongoing evaluation, updating and statistical treatment. Experts in groundwater science, agricultural chemistry and related study areas will be consulted to critique work plans, data and information, and conclusions.

B.1.b. Methods: All relevant information and data will be collected, organized and stored in hard files and computer database files as the study progresses. Datafiles utilizing Paradox and Foxpro database management software will be maintained for frequent review and analysis. Statistical treatment of appropriate data will be accomplished utilizing several formats and models available on SPSS+ software or its equivalent. Harvard Graphics and other software will be used for rendering diagrammetric and graphic data. Specific data for sites in Dakota County will be transferred to the County's ARC/INFO Geographic Information System (GIS), and similar data for other counties may be transferred to similar GIS programs at the state or appropriate county level.

B.2.c. Materials: This objective is accomplished utilizing existing hard file storage and computer databases and software (Paradox, Foxpro, Harvard Graphics, ARC/INFO GIS, ARC/VIEW, etc.).

B.1.d. Budget: $25,000.
Balance: $10,405

| B.1.e. Timeline: | 7/93 | 1/94 | 6/94 | 1/95 | 6/95 |
|---|---|---|---|---|---|
| Classify/enter datafiles | | | ********************************** | | |
| Conduct statistical calc | | | ***************************************** | | |
| Create ARC/INFO GIS | | | | ********************* | |
| Complete study evaluation | | | | | ***** |

B.2. Status:

B.2.a. Problems and Progress:

As previously reported, the program manager determined that Microsoft Office Plus for Windows was the most practical software package for the multiple computer tasks required by the project, and it was recently supported by the Dakota County Data Processing Department to integrate it with the existing Foxpro software-based database management programs that were recently upgraded. In particular, the County's Geographic Information System (GIS) which is written in ARC/INFO and ARC/VIEW will be accessible via Foxpro and Microsoft Office Plus's "Access", a user friendly relational database management system which is compatible. The design will be similar to and compatible with the information management system for the LMIC. However, development, as well as data entry, is still underway.

In 1996, continuing computer hardware and software modifications have been made which favor individual personal computer/local area network supported programs rather than mainframe or wide area network programs. The Dakota County GIS is now being written in ARC/VIEW and supporting relational databases are being written in Microsoft Access and SQL. The ten study areas in Dakota County are incorporated in a countywide, integrated GIS/Database Management System effort led by the Survey and Information Department which works closely with the Environmental Management Department on developmental issues.

V. Evaluation

For the FY94-95 biennium, the study may be evaluated by: 1.) The extent and completion of field work in the nine-county area; 2.) The completion of laboratory analyses of optical brighteners, background parameters, pollution indicators and contaminants of concern or interest (e.g., nitrate-nitrogen and triazine herbicides); and 3.) The ongoing analysis and completed evaluation of study information and data.

In the long-term, the study may be evaluated by its utility in aiding environmental science practitioners (regulatory, academic and industry) with their understanding and evaluation of domestic sewage contamination of groundwaters. If successful in discovering that optical brighteners may be implicated in the false positive detections of triazine herbicides in groundwaters, the study would resolve some problems previously noted in other investigations.

VI. Context Within Field

To date, the specific impact of domestic sewage on the contamination of groundwaters in Minnesota and elsewhere is unknown. Due to the ubiquity of nitrogen (e.g., nitrates) and other sewage parameters in the environment, isotopic nitrogen analyses have been only marginally successful in identifying contamination sources in agricultural areas. However, such assays are cost-prohibitive and unavailable to the majority of workers and researchers.



The inability to identify nitrogen and other contaminant sources in impacted groundwaters makes it difficult to target the actual primary sources and affectuate remedies. In particular, owners of sewage systems in agricultural areas blame farmers for the elevated nitrates in their water supplies, and such a bias impedes regulators from adopting regulations and zoning ordinances where the sources of the contamination cannot be proven.

Regulators and researchers alike have noted the prevalence of triazine (especially, atrazine) herbicide residues in the groundwaters of agricultural areas. However, some researchers have noted positive detections of atrazine in areas where little or no atrazine had reportedly been used. Such potential false positive detections create difficulties in assessing the true extent and impact of triazine herbicide contamination of groundwaters. With the advent of state bans or restrictions on their use and the employment of best management practices where still permitted to be used, atrazine and other triazine herbicides may be unduly restricted in some environments where false positive tests are prevalent.

The study will focus on research needs in the above described areas with potentially significant results being immediately transferrable to the environmental practitioner and land owner. In particular, the study results, whether positive or negative, will be shared with the Minnesota Department of Agriculture and the University of Minnesota research staffs working on related legislative studies and initiatives.

VII. Benefits

The study may be applicable to most of Minnesota and will benefit groundwater protection planning and implementation as domestic sewage systems and agricultural fertilizer and herbicide use are the two most significant non-point sources of contaminants recognized statewide. The utility of a passive, conservative tracer of domestic sewage contamination would be a useful tool for the environmental practitioner and researcher. They may be able to ascertain the approximate proportion of a common contaminant, such as nitrate, that is related to domestic sewage systems by determining optical brightener concentrations in groundwater. Depending upon the location and the aquifer, statistically significant regression analyses of nitrate-nitrogen (or another contaminant) concentration on optical brightener concentration may allow a reasonable interpretation of the impact of domestic sewage on drinking water supplies. In contrast, the unrelated concentration of nitrate (or another contaminant) may then be attributable to other non-domestic sewage sources. Such results may be used to target potential contamination sources more precisely focusing mitigative measures and other location-specific solutions (zoning, sewage system requirements, agricultural best management practices, etc.).

The use of a cotton detector for optical brightener screening of domestic sewage contaminants would be an effective, economic tool for the sanitary evaluation of drinking water supplies that presently rely upon only two sanitary parameters, namely total coliform bacteria and nitrate-nitrogen. It is known that acceptable results for either of those sanitary tests are possible even if the water supply is contaminated with domestic sewage because of several factors. If standard sanitary testing were to incorporate both specific conductance testing and optical brightener screening as well, there would be less chance of not identifying possible domestic sewage-contaminated water supplies. In the repertory of environmental health professionals, such minmum requirements for sanitary testing would help identify problems and prevent disease for an unprotected segment of individual water supply consumers.

Given the apparent prevalence of atrazine in the groundwaters of Minnesota, significant legislation, regulatory action and agricultural consumption has diminished or restricted its use. If the study determines that some of the false positive testing of atrazine or other triazine herbicides may have been the result of interferences from or alternatively false detections of optical brighteners, the research and corrective actions related to triazine herbicides may be improved and beneficial to all parties.

## VIII. Dissemination

During and after the field and laboratory phases of the study, peers in regulatory agencies and academic institutions will be kept apprised of interim and final results and evaluations to elicit critical review to improve the study and to transfer any substantive findings that may have immediate value requiring test replication for verification.

In addition, formal and informal dissemination to others working in the area, including zoning administrators, planners, water resource managers, county extension agents and water supply/treatment professionals, will be encouraged where the results may be put to practical use.

Depending upon the results and conclusions, the study's findings will be presented formally at local, state and national scientific meetings attended by peers in associated disciplines. Additionally, presentations and papers will be submitted for publication by peer-reviewed, professional journals to ensure a wide audience and promote related investigations to verify the results and conclusions of the research elsewhere.

The study data will be stored in Paradox and Foxpro datafiles, some transferred to the County's ARC/INFO GIS and otherwise available for sharing with related databases at the state and municipal level for beneficial use. The datafiles will be coordinated with the Land Management Information Center for statewide utilization through IGWIS and associated information management systems and databases as needed.

The importance of some of the possible findings of the study may lead to local and state regulatory changes, especially in the recognition of definitive methods for defining impacts from domestic sewage systems (land use zoning, individual sewage treatment system standards, well construction and sealing standards, safe drinking water standards, etc.) and the identification of false positive detections of triazine herbicides. The findings will be disseminated to state legislators and municipally elected officials as appropriate to any recommendations for changes to existing laws.

## IX. Time

The purview and intent of the study are to be completed within the FY94-95 biennium.

## X. Cooperation

Informal cooperation with peers in state and municipal regulatory agencies (e.g., Minnesota Department of Health, Minnesota Department of Agriculture, Minnesota Department of Natural Resources, Minnesota Pollution Control Agency, Minnesota Board of Water and Soil Resources, county public health departments and county planning and zoning offices), state academic institutions



(University of Minnesota, Minnesota Extension Service and Winona State University) and others will be maintained throughout the study for coordination, guidance and critical review. No specific cooperators have been established.

## XI. Reporting Requirements

Semiannual status reports will be submitted not later than January 1, 1994, July 1, 1994, and January 1, 1995, and a final status report will not be submitted later than June 30, 1995.

## XII. Pertinent Literature


Alhajjar, B.J., G. Chesters, and J.M. Harkin, 1990, "Indicators of chemical pollution from septic systems", Ground Water, 28 (4): 559-568.

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Fay, Steffan R., E. Calvin Alexander, Jr., and Ronald C. Spong, 1994, "Optical brighteners as indicators of septic system pollution in water-table aquifers of southeastern Minnesota", Abstract in Proceedings of the American Water Resources Association, Conference, November 8, 1994, in Chicago, Illinois.

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Fay, Steffan, 1996, Plan B Papers, Master of Science Degree, University of Minnesota, Geology and Geophysics Department:

1. "Occurrence of Optical Brighteners in Shallow Unconfined Aquifers of Southeastern Minnesota."
2. "Sorption Behavior of Optical Brighteners."
3. "Detection of Optical Brighteners with Polyethersulfone Filter Media."

Smart, Peter L., and I.M.S. Laidlaw, 1977, "An evaluation of some fluorescent dyes for water tracing", Water Resources Research, 13(1): 15-33.

Spong, Ronald C., Steffan R. Fay and E. Calvin Alexander, Jr., 1995, "Optical brightener screening for sewage contamination of water table aquifers in southeastern Minnesota, USA", Proceedings of the XXVI Congress of the International Association of Hydrogeologists, June 4-10, 1995, Edmonton, Alberta, Canada.

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# ATTACHMENT 1

# OPTICAL BRIGHTENER DETECTION METHODOLOGY AND RESULTS SUMMARY

**Steffan Fay**
University of Minnesota, Dept. of Geology & Geophysics

## 1.0 INTRODUCTION

This attachment describes methodologies developed for the detection of optical brighteners and presents a breakdown of the results of analysis of field samples. Field samples were grouped into batches based on submittal date. The summaries presented herein are based on the results of samples up to and including those in batch 38 (submitted June 2, 1995). The findings should therefore be considered somewhat preliminary, and will be revised and updated for the final project report.

## 2.0 METHODS

Optical brighteners can be detected using a spectrofluorophotometer. The spectroflorophotometer measures the light emitted from a sample at a specified wavelength or range of wavelengths when excited by light at another (shorter) wavelength or range of wavelengths. The fluorometer used was a Shimadzu RF5000U (Shimadzu Corporation, Kyoto, Japan).

The optical brightener detection methodologies employed in this study can be separated into two broad categories: detection in direct solution and detection on a solid medium. In the course of the study we have investigated optical brighteners in water, sorbed to unbrightened cotton, and sorbed to polyethersulfone filter media.

A microcomputer was used to control the fluorometer remotely and facilitate the electronic storage of fluorescence spectra. The analytical methodology developed during the course of the project entailed the use of three individual scans per sample, corresponding to the three scan modes of the fluorometer. The three scan types are as follows:

1) Synchronous scan. Excitation and emission wavelengths are varied by the fluorometer keeping a constant separation ($\Delta\lambda$).

2) Excitation scan. Emission wavelength is held at a specified value. Excitation wavelength is varied.

3) Emission scan. Excitation wavelength is held at a specified value. Emission wavelength is varied.



### 2.1 List of Materials

**2.1.1 Cotton Pads:**
Target brand.
Johnson & Johnson brand.

**2.1.2 Filter Media:**
Gelman Corporation. Ann Arbor, Michigan.

**2.1.3 Optical Brighteners:**
Tinopal 5BM-GX. Commercial grade. Batch #1009.
Ciba-Geigy Corporation. Greensboro, North Carolina.

Tinopal CBS-X. Commercial grade. Batch #34918038.
Ciba-Geigy Corporation. Greensboro, North Carolina.

**2.1.4 Laundry Detergents:**
Purex Ultra powder. Dial Corporation. Phoenix, Arizona.
All liquid. Lever Bros. New York, New York.
Woolite liquid. Reckitt & Colman. Wayne, New Jersey.
Cheer powder. Proctor & Gamble. Cincinnati, Ohio.
Tide Ultra powder. Proctor & Gamble. Cincinnati, Ohio.
Tide Ultra liquid. Proctor & Gamble. Cincinnati, Ohio.
Fab Ultra powder. Proctor & Gamble. Cincinnati, Ohio.

### 2.2 Sample Handling and Preparation

Direct samples were collected and stored in brown glass bottles. All samples were stored refrigerated in total darkness until analysis. Direct samples were analyzed in a 5 ml acrylic cuvette. Solid samples were analyzed in the fluorometer solid sample holder. Solid samples were left damp or dampened with deionized water prior to analysis to reduce scattering of excitation light.

## 3.0 RESULTS

### 3.1 Optimum Settings

The detection of optical brighteners requires the visual recognition of characteristic peaks in the fluorescent spectra of samples. Based on the results of analyses of laboratory prepared optical brightener standards and laundry detergents both in solution and sorbed to cotton, the following RF5000U fluorometer settings were found to be optimum for the detection of optical brighteners (and optical brighteners):

#### 3.1.1 Direct Solution

Sensitivity: high
Band width: 3 nm
Synchronous scan: $\Delta\lambda = 95$ nm, vary emission wavelength between 320 nm & 520 nm
Excitation scan: Emission wavelength = 440 nm,
vary excitation wavelength between 240 nm & 430 nm
Emission scan: Excitation wavelength = 345 nm,
vary emission wavelength between 355 nm & 570 nm

The presence of optical brighteners is indicated by peaks at the following wavelengths:
Synchronous scan: 440 nm
Excitation scan: 345 nm
Emission scan: 440 nm

#### 3.1.2 Sorbed to Cotton

Sensitivity: high
Band width: 3 nm
Synchronous scan: $\Delta\lambda = 60$ nm, vary emission wavelength between 350 nm & 550 nm
Excitation scan: Emission wavelength = 440 nm,
vary excitation wavelength between 300 nm & 430 nm
Emission scan: Excitation wavelength = 380 nm,
vary emission wavelength between 390 nm & 550 nm

The presence of optical brighteners is indicated by peaks at the following wavelengths:
Synchronous scan: 440 nm
Excitation scan: 380 nm
Emission scan: 440 nm

#### 3.1.3 Sorbed to Polyethersulfone

Sensitivity: high
Band width: 1.5 nm
Synchronous scan: $\Delta\lambda = 65$ nm, vary emission wavelength between 375 nm & 575 nm
Excitation scan: Emission wavelength = 435 nm,
vary excitation wavelength between 300 nm & 430 nm
Emission scan: Excitation wavelength = 370 nm,
vary emission wavelength between 380 nm & 525 nm

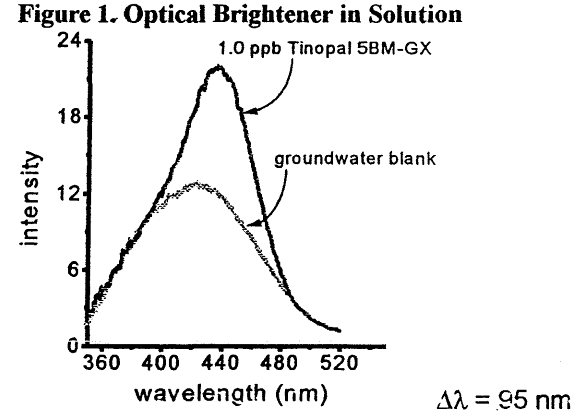


The presence of optical brighteners is indicated by peaks at the following wavelengths:
Synchronous scan: 435 nm
Excitation scan: 370 nm
Emission scan: 435 nm

### 3.2 Detection in Direct Solution

Optical brighteners can be detected in solution. However, naturally occurring organic compounds present even in pristine groundwaters fluoresce at similar wavelengths causing interference at low optical brightener concentrations. Figure 1 contains synchronous scans of a pristine groundwater and of a 1.0 ppb solution of an optical brightener in groundwater. The interference problem is further compounded by the variability of natural groundwater fluorescence.

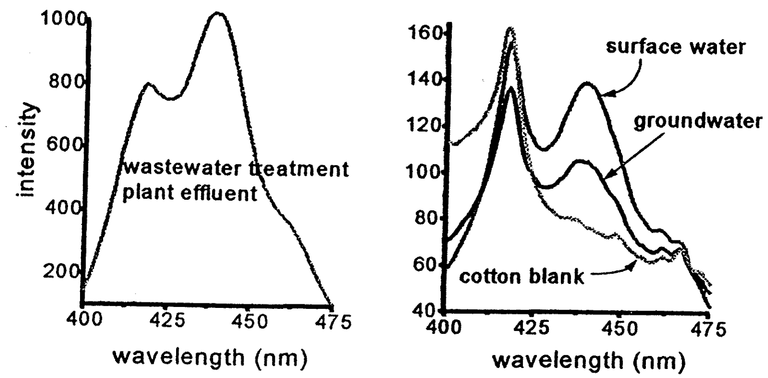
**Figure 1. Optical Brightener in Solution**




### 3.3 Detection on Cotton

Cotton immersed in water streams containing optical brighteners obtain peaks at wavelengths characteristic of optical brighteners and laundry detergents. Figure 2 contains some scans of samples considered positive for optical brighteners. The samples were exposed to various water environments. All of the spectra in figure 2 are synchronous scans ($\Delta\lambda = 60$ nm) of cotton samples. Note that the graph on the left side of figure 2 (cotton after exposure to the effluent stream of a waste water treatment plant) has a much larger y axis, indicating a greater degree of brightening.

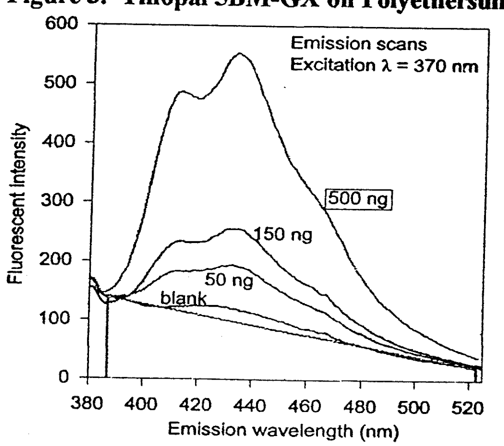
**Figure 2. Example Fluorescence Spectra of Cotton Samples Positive for Optical Brighteners**




### 3.4 Detection on Polyethersulfone

Optical brighteners accumulate on polyethersulfone filter membrane material. Figure 3 contains fluorescent spectra of filter media with various masses of optical brightener applied. Optical brighteners were applied to the filter medium using a syringe connected to a syringe tip filter. Optical brighteners produce peaks at characteristic wavelengths in the fluorescent spectrum of polyethersulfone. The area beneath the peaks increases with increasing sorbed mass of optical brighteners.

**Figure 3. Tinopal 5BM-GX on Polyethersulfone Filter Medium.**






### 3.5 Field Sampling Program Results Summary

Within field sample batches 1 through 38, cotton based immersion detectors appear to have functioned better than other detection methodologies. This section is a summary of the results of batches 3 through 38 inclusive. Batches 1 and 2 are not contained in this summary because detection parameters had not been optimized at the time of analysis. Cotton samples from batches 3 through 38 were analyzed in accordance with the settings described in section 3.1.2, with the exception of some samples being scanned with fluorometer band widths set at 5 nm rather than 3 nm. Table 1 contains a summary of sample submissions organized by batch number.

Each sample was analyzed at one or more locations on the surface of the cotton pad. This was achieved by repeatedly analyzing the cotton pad, and moving it around in the sample holder between scans. This methodology was followed in an attempt to address heterogeneity with respect to brightening across the surface of the pad.

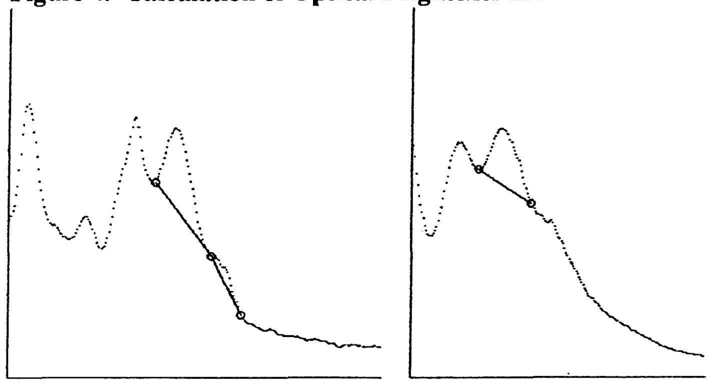
Following fluorometric analysis a hard copy output was generated. Hard copy outputs were used to visually asses the sample fluorescence spectrum for the presence of characteristic peaks. If no peak above background at 440 nm in the synchronous scan was discernible the sample scan was designated N (negative). The observation of a peak at 440 nm caused the sample to be designated P (positive). In cases where the presence or absence of a peak could not easily be established a designation of I (indeterminable) was applied.

Fluorescence spectra were processed with a computer algorithm to calculate the ratio between peaks characteristic of optical brighteners to a set of peaks present in both blanks and positive samples. The term "optical brightener index" (OBI) is used to describe the ratio of specific optical brightener characteristic peak areas to specific background peak area. Figure 4 illustrates how the peak areas and OBI are calculated with an example. The OBI serves to quantify the size of the optical brightener peak and normalizes the optical brightener peak to the magnitude of the background peaks. Relatively larger characteristic optical brightener peaks produce larger values of OBI. Background portions of exposed sample scans vary over a wide range as a result of cotton surface contamination with bacterial deposits and solid particles.

The optical brightener index was calibrated to the visual observations of peak presence. The value of OBI which corresponded best to apparent visual cutoff between positive and indeterminable was 3.2. Table 2 is a summary of field sample analyses including visual classification and OBI for all scans.

Individual scan OBIs were then averaged to produce an overall sample OBI. Figure 5 combines OBI information (y axis, log scale) with exposure time information. Exposure time is defined as the length of time cotton immersion sample were in place in the field. The horizontal line at OBI = 3.2 represents the cutoff between positive and negative based on OBI.

**Figure 4. Calculation of Optical Brightener Index**



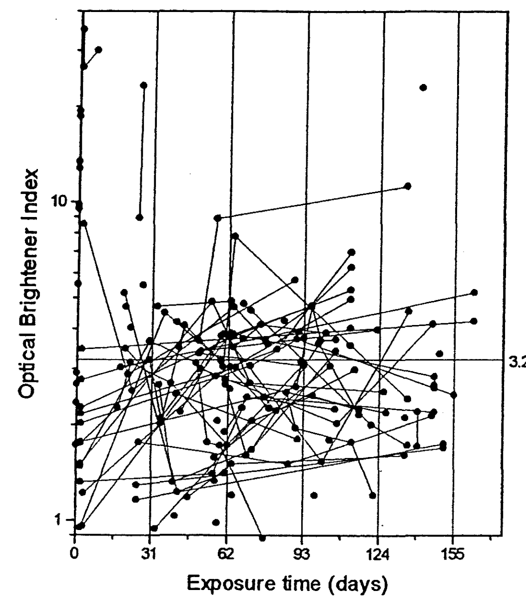
B:\BATCH21\1021EF6.FWA
AREA1: 1256.958 AREA2: 193.7675 AREA3: 995.9684

AREA1/AREA2: 6.486943 (AREA3+AREA1)/AREA2: 11.62692

Notes: Left pane = synchronous scan
Right pane = emission scan
Areas are numerically integrated between sloping straight line and signal
Area 1 = characteristic optical brightener peak in synchronous scan
Area 2 = background peaks
Area 3 = characteristic optical brightener peak in emission scan
Optical brightener index = (Area1 + Area3) / Area2



**Figure 5. Optical Brightener Index vs Exposure time**

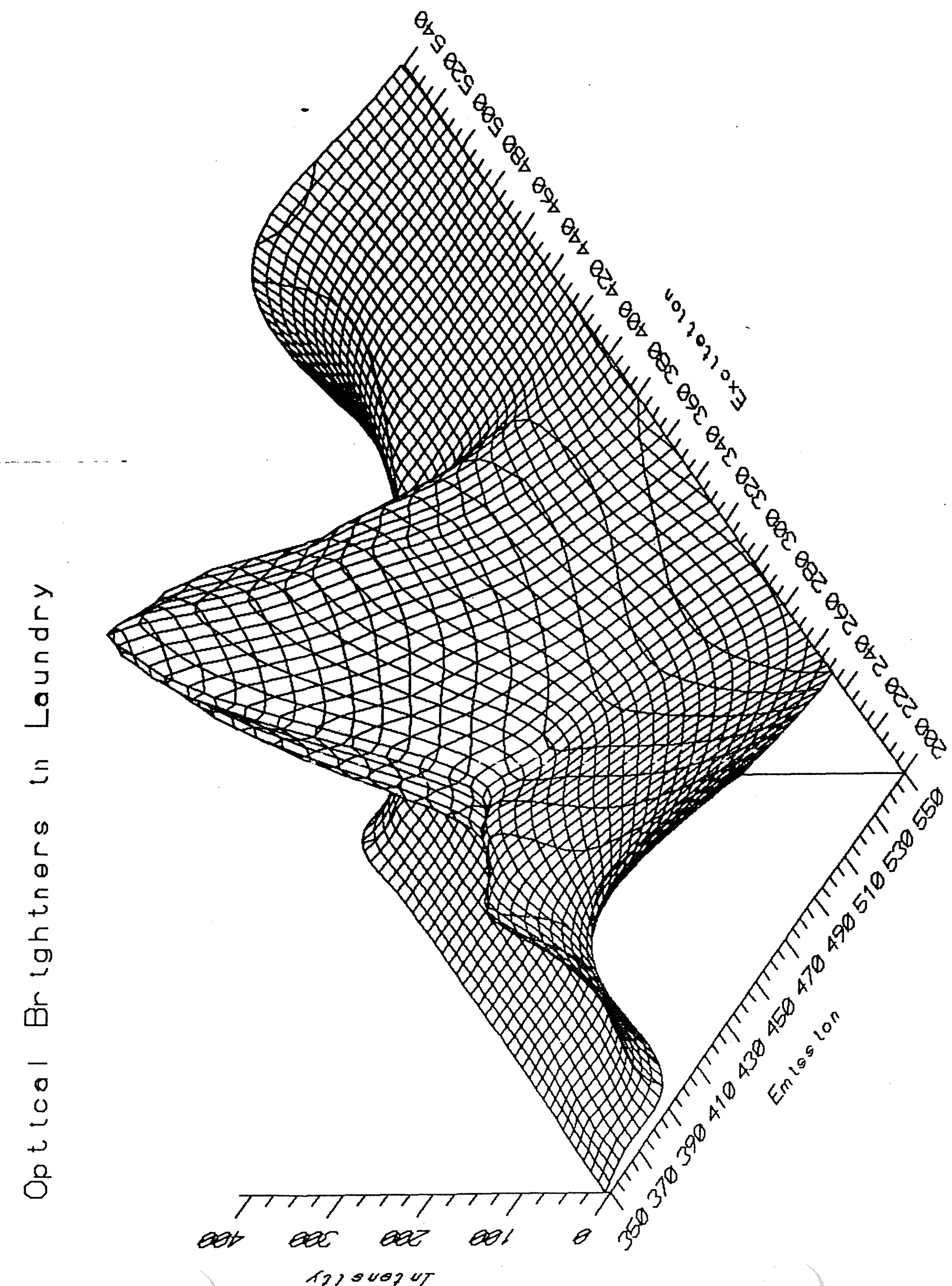



Notes: Dots = individual samples
Lines connect samples from the same location

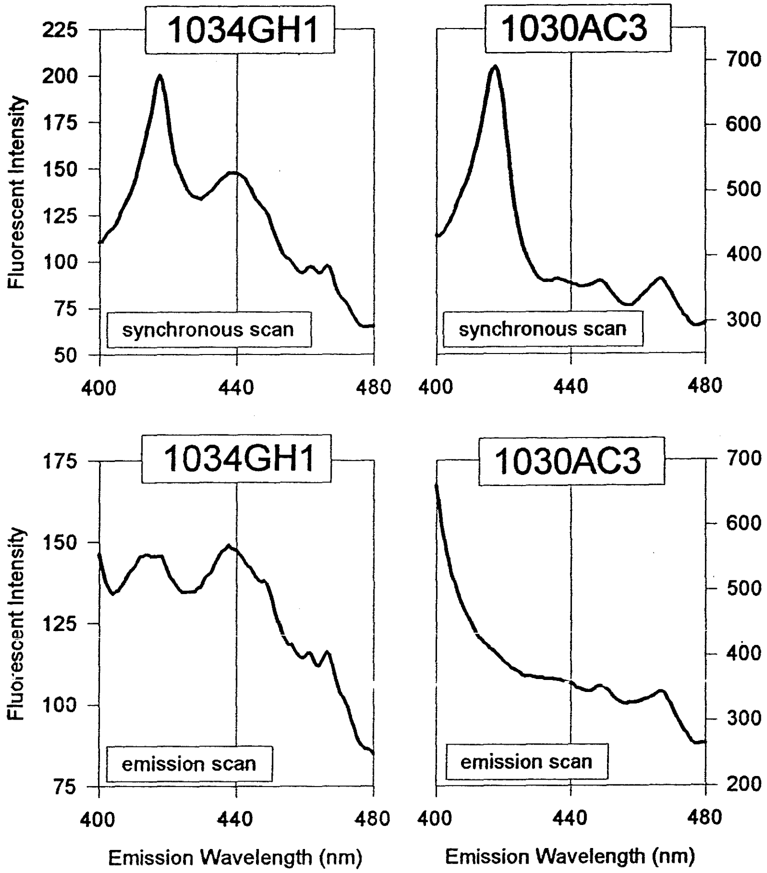
**Table 1. SOUTHEASTERN MINNESOTA COMMUNITIES SELECTED FOR STUDY**

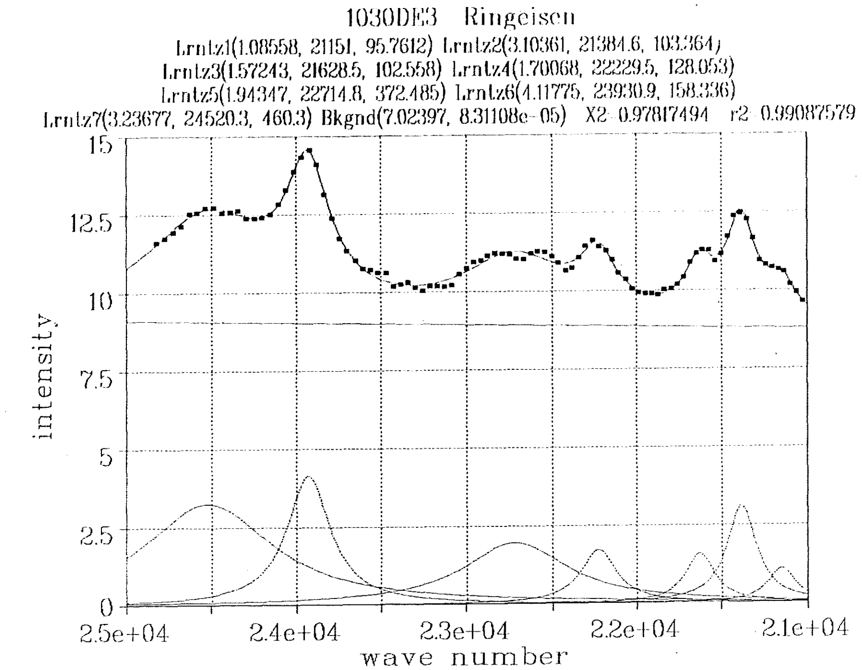
| COUNTY | COMMUNITY | HYDROGEOLOGIC SETTING |
|---|---|---|
| 1 DAKOTA | 10 - CASTLE ROCK (unincorp.) & CASTLE ROCK, WATERFORD TWP | Pre-Wisc morraine/outwash-mantled sandstone (eroded) on dolostone. Till/outwash/rock aquifer (WT 10-50 ft.). |
| | 11 - COATES & ROSEMOUNT (east) | Wisc. outwash-mantled dolostone (anticline striking 300°). WT aquifer at 70-90 ft. near outwash/rock contact. |
| | 12 - EMPIRE CITY (unincorp.) & VERMILLION TWP | Alluvium, Wisc. outwash-filled buried dolostone valley (200-300 ft. trending ENE). Valley fill aquifer (WT at 10-30 ft.). |
| | 13 - FARMINGTON & EMPIRE TWP | Alluvium, Wisc. outwash-filled buried sandstone/dolostone valley (50-200 ft. NE). Valley fill aquifer (WTat 10-30 ft.). |
| | 14 - HAMPTON TWP | Mixed till, slopewash-mantled, eroded sandstone/dolostone (folded/faulted in vicinity). Bedrock aquifer (WT 50-150 ft.). |
| | 15 - HASTINGS | Alluvium, residual Wisc. till/outwash-mantled dolostone (eroded, folded/faulted blocks) isolated by filled sluiceways. Karsted, fractured rock or fill aquifer (WT at 10-100 ft.). |
| | 16 - Separate Sites: MARSHAN TWP & INVER GROVE HEIGHTS (IGH) | Marshan: Wisc outwash-mantled dolostone (WT 80-150 ft.) IGH: Wisc. till/outwash-mantled dolostone (WT 50-200 ft.). |
| | 17 - MIESVILLE & DOUGLAS TWP | Pre-Wisc. till/loess-mantled, dolostone/sandstone aquifer (WT 50-150 ft.). Covered karst with no surface streams. |
| | 18 - NININGER (unincorp.) & NININGER TWP | Alluvium & Wisc. outwash valley fill & mantled dolostone & sandstone aquifers (WT 25-200 ft.). Fault blocks in area. |
| | 19 - ROSEMOUNT (north) | Thick Wisc. till-mantled, eroded sandstone/dolostone. Till aquifer with WT 15-30 ft. Area wetlands with lakes/ponds. |
| 2 DODGE | 20 - None | Several areas scouted near Concord, Berne & Mantorville. Other study commitments pre-empted completion. |
| 3 FILLMORE | 30 - CANTON & CANTON TWP | Pre-Wisc. till/loess-mantled, karsted carbonate rock aquifer (WT 25-150 ft). Canton WWTP effluent sinks below outfall. |
| | 31 - FAIRVIEW (unincorp.) & FORESTVILLE TWP | Pre-Wisc. till/loess-mantled, maturely karsted carbonate rock aquifer (WT 90-150 ft.). Flow east traced to springs. |
| | 32 - FILLMORE (unincorp.) & FILLMORE TWP | Alluvium, slopewashed till/loess valley fill & limestone/sandstone aquifers (WT 25-50 ft.). Losing streams in vicinity. |
| | 33 - FOUNTAIN TWP | Pre-Wisc. till/loess-mantled, karsted carbonate rock aquifer (WT 70-120 ft). Traced streamflows oriented by folds/faults. |
| | 34 - NEWBURG (unincorp.) & NEWBURG TWP | Thin pre-Wisc. till/loess-mantled, karsted dolostone aquifer (WT 50-100 ft.). Springs downgradient of communities. |
| | 35 - WASHINGTON (unincorp.) & SUMNER TWP | Pre-Wisc. till (morraine)/loess-mantled, karsted carbonate rock aquifer (WT 25-120 ft). Distributary springs in syncline |
| 4 GOODHUE | 40 - VASA (unincorp.) & VASA TWP | Pre-Wisc. till/loess-mantled, eroded sandstone/dolostone aquifer (WT 40-130 ft.). Shallow wells, cisterns still in use. |
| 5 HOUSTON | 50 - SPRING GROVE | Pre-Wisc. till/loess-mantled ridge of shale-capped limestone & sandstone aquifer (WT 25-100 ft). City well contaminated. |
| 6 MOWER | 60 - None | Several areas scouted near Racine and Le Roy. Other study commitments pre-empted completion. |
| 7 OLMSTED | 70 - MARION (unincorp.) & MARION TWP | Alluvium, slopewashed till/loess valley fill & eroded shale & limestone aquifers (WT 10-50 ft.). Downstream wetlands. |
| | 71 - PLEASANT GROVE (unincorp.) & PLEASANT GROVE TWP | Thick (50+ ft.) pre-Wisc. till/loess & carbonate rock aquifers (WT 25-150 ft.). Wells completed in deeper rock aquifer. |
| | 72 - SIMPSON (unincorp.) & PLEASANT GROVE TWP | Thick pre-Wisc. till/loess & carbonate rock aquifers (WT 20-100 ft). Wells completed in shallow and deeper aquifers. |
| 8 WABASHA | 80 - CHESTER & GILLFORD TWP (upgradient of Zumbro Falls) | Pre-Wisc. till/loess-mantled dolostone aquifer with folded & faulted rock in vicinity (WT 20-100 ft.). Artesian springs. |
| 9 WINONA | 90 - SARATOGA (unincorp.) & SARATOGA TWP | Pre-Wisc. till/loess-mantled, eroded sandstone/dolostone aquifer (WT 15-50 ft.). Artesian springs suggest syncline. |

NOTES: Abbreviations - TWP = Township; (unincorp.) = unincorporated community; Pre-Wisc. & Wisc. = pre & collateral Wisconsinan glacial deposits; WT = [illegible]er table aquifer.



# Coates




1030DE3 Ringeisen Dec 14,1994 6:27 PM
92 Active X-Y Points
X: wave number Mean: 22822.24163 SD: 1113.1365918
Y: intensity Mean: 11.284217391 SD: 1.0854002232
File Source: 1030DE3.PRN
Curve-Fit Std Error= 0.119064892 r2= 0.990875789

Background Coefficients [y=a+bx+cx^2+dx^3]

| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | 7.0239735 | 8.311e-05 | | |

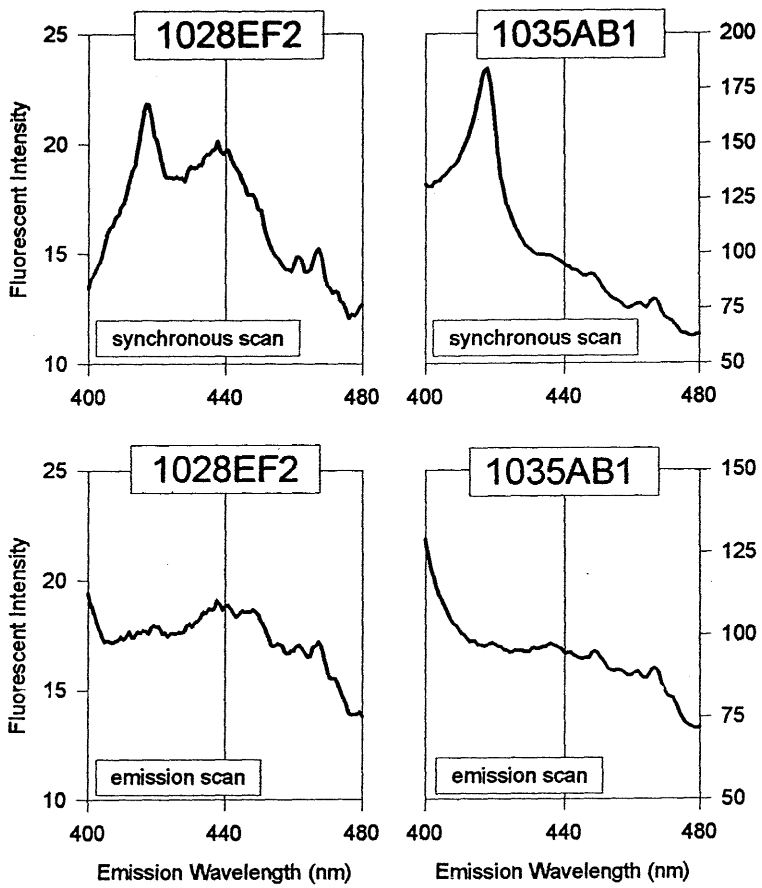
Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.085576 | 2.115e+04 | 95.761167 | | |
| 2 | Lorentzian | 3.1036094 | 2.138e+04 | 103.36367 | | |
| 3 | Lorentzian | 1.5724271 | 2.163e+04 | 102.55848 | | |
| 4 | Lorentzian | 1.7006846 | 2.223e+04 | 128.05336 | | |
| 5 | Lorentzian | 1.9434662 | 2.271e+04 | 372.48496 | | |
| 6 | Lorentzian | 4.1177509 | 2.393e+04 | 158.33632 | | |
| 7 | Lorentzian | 3.2367666 | 2.452e+04 | 460.30009 | | |

Measured Values

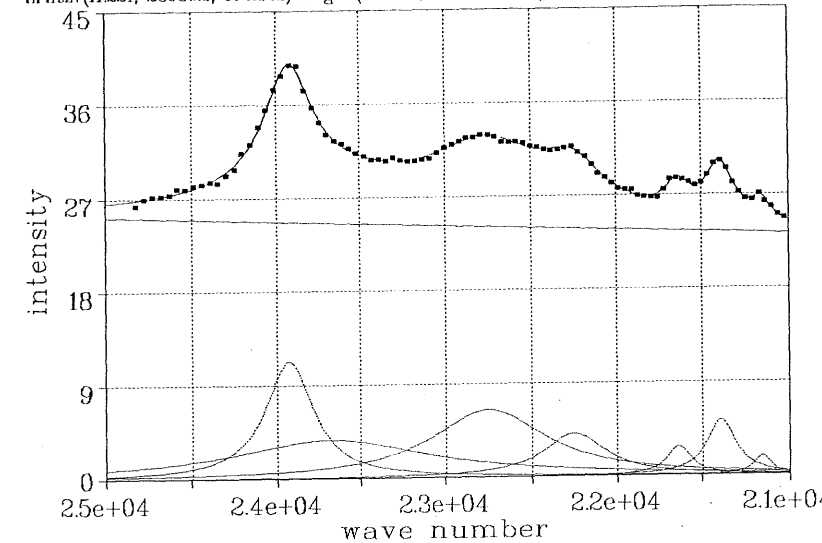
| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.085576 | 2.115e+04 | 191.52125 | 255.83734 | 2.7816802 |
| 2 | Lorentzian | 3.1036094 | 2.138e+04 | 206.72643 | 908.1232 | 9.8738846 |
| 3 | Lorentzian | 1.5724271 | 2.163e+04 | 205.11547 | 474.26371 | 5.1565968 |
| 4 | Lorentzian | 1.7006846 | 2.223e+04 | 256.10433 | 650.35151 | 7.0711725 |
| 5 | Lorentzian | 1.9434662 | 2.271e+04 | 744.96719 | 1990.6671 | 21.644219 |
| 6 | Lorentzian | 4.1177509 | 2.393e+04 | 316.67024 | 1898.6687 | 20.643934 |

## Empire City




1038CD3 Willing

Lrntz1(1.7754, 21155.4, 58.1342) Lrntz2(5.28887, 21390.8, 100.543)
Lrntz3(2.74946, 21639.6, 87.8989) Lrntz4(4.06749, 22252.2, 219.901)
Lrntz5(6.44162, 22750.1, 402.277) Lrntz6(3.66903, 23675.6, 721.142)
Lrntz7(11.221, 23930.5, 174.332) Bkgnd(12.9139, 0.000489489) X2=3.5490454 r2=0.99595407




1038CD3 Willing — Dec 14,1994 6:31 PM

92 Active X-Y Points

X: wave number — Mean: 22822.24163 — SD: 1113.1365918

Y: intensity — Mean: 30.263880435 — SD: 3.1047429893

File Source: 1038CD3.PRN

Curve-Fit Std Error= 0.226793829 — r2= 0.995954065

Background Coefficients [y=a+bx+cx^2+dx^3]

| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | 12.913865 | 0.0004895 | | |

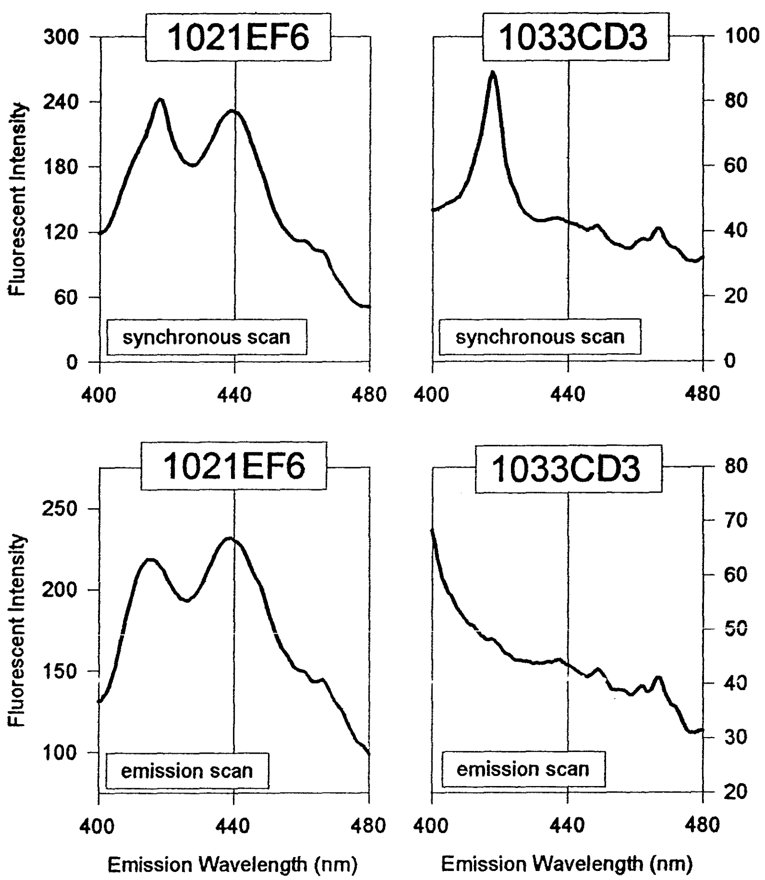
Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.7753974 | 2.116e+04 | 58.13421 | | |
| 2 | Lorentzian | 5.2888663 | 2.139e+04 | 100.54258 | | |
| 3 | Lorentzian | 2.7494626 | 2.164e+04 | 87.898859 | | |
| 4 | Lorentzian | 4.067489 | 2.225e+04 | 219.90139 | | |
| 5 | Lorentzian | 6.4416228 | 2.275e+04 | 402.2773 | | |
| 6 | Lorentzian | 3.6690306 | 2.368e+04 | 721.14172 | | |
| 7 | Lorentzian | 11.220995 | 2.393e+04 | 174.3322 | | |

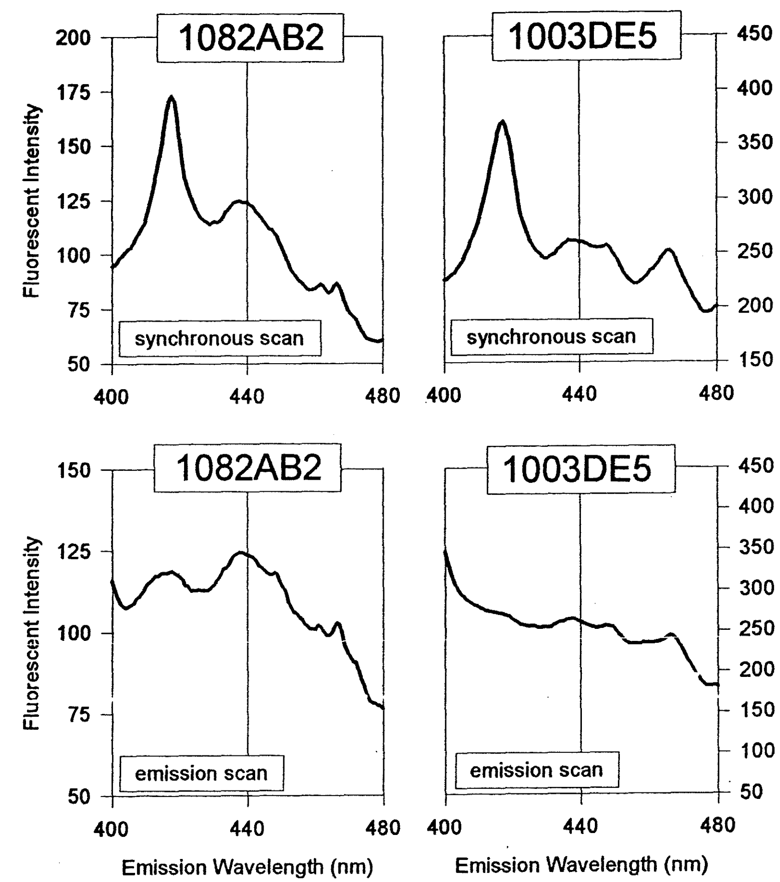
Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.7753974 | 2.116e+04 | 116.26673 | 278.97718 | 1.16653 |
| 2 | Lorentzian | 5.2888663 | 2.139e+04 | 201.08457 | 1511.9268 | 6.3220509 |
| 3 | Lorentzian | 2.7494626 | 2.164e+04 | 175.79724 | 718.18161 | 3.0030427 |
| 4 | Lorentzian | 4.067489 | 2.225e+04 | 439.80162 | 2575.0156 | 10.767307 |
| 5 | Loren[illegible]n | 6.4416228 | 2.275e+04 | 804.55228 | 705[illegible]969 | 29.482994 |
| 6 | Loren[illegible]n | 3.6690306 | 2.368e+04 | 1442.2814 | 61[illegible]38 | 25.623625 |

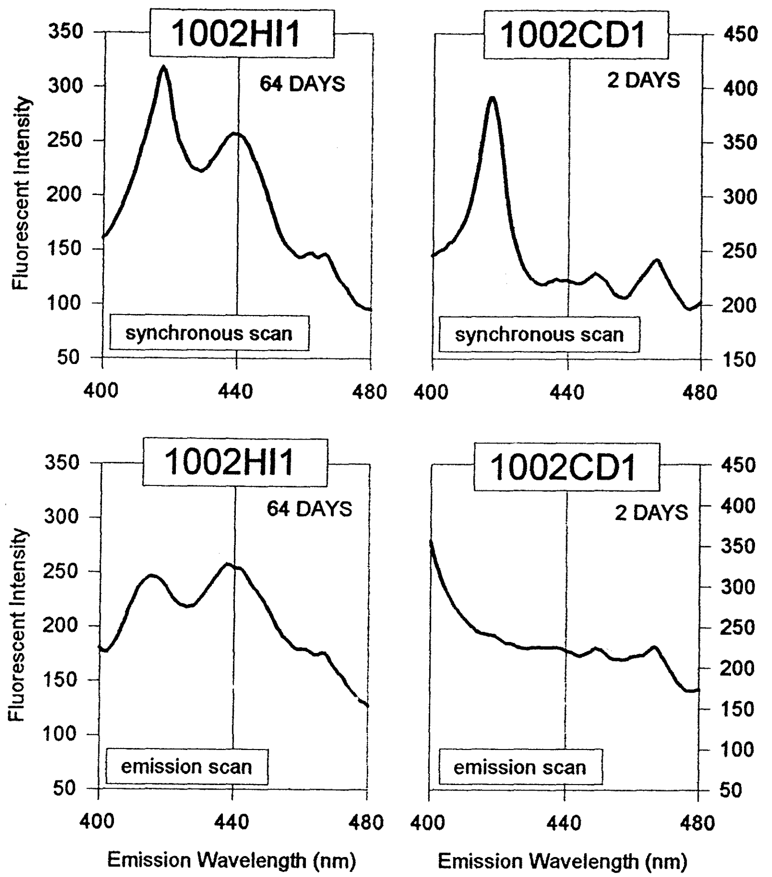
# Castle Rock



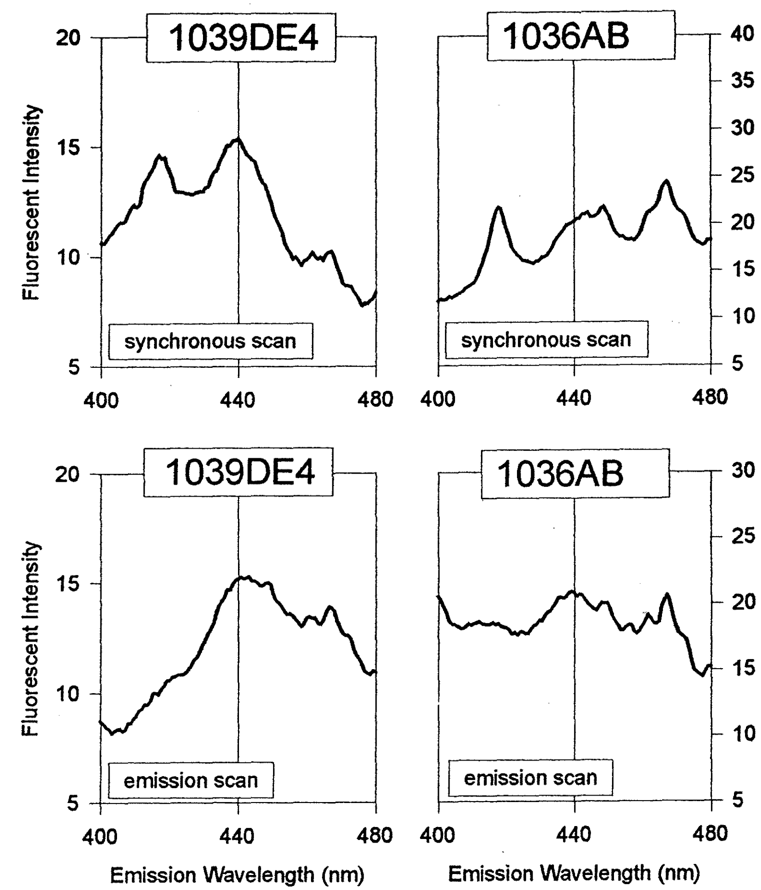

# Farmington



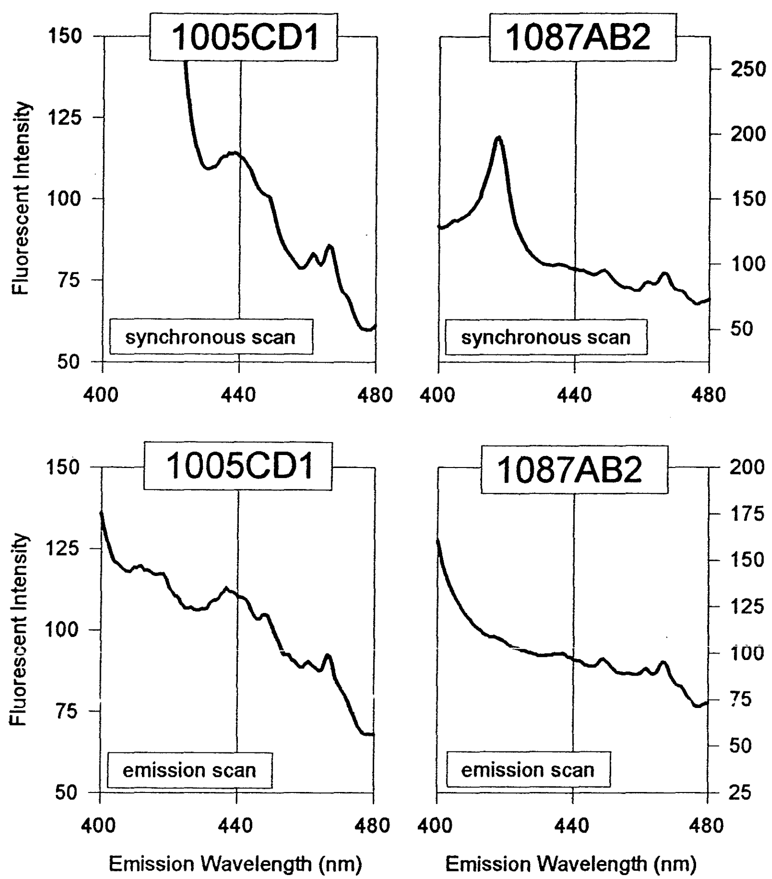
# Hampton



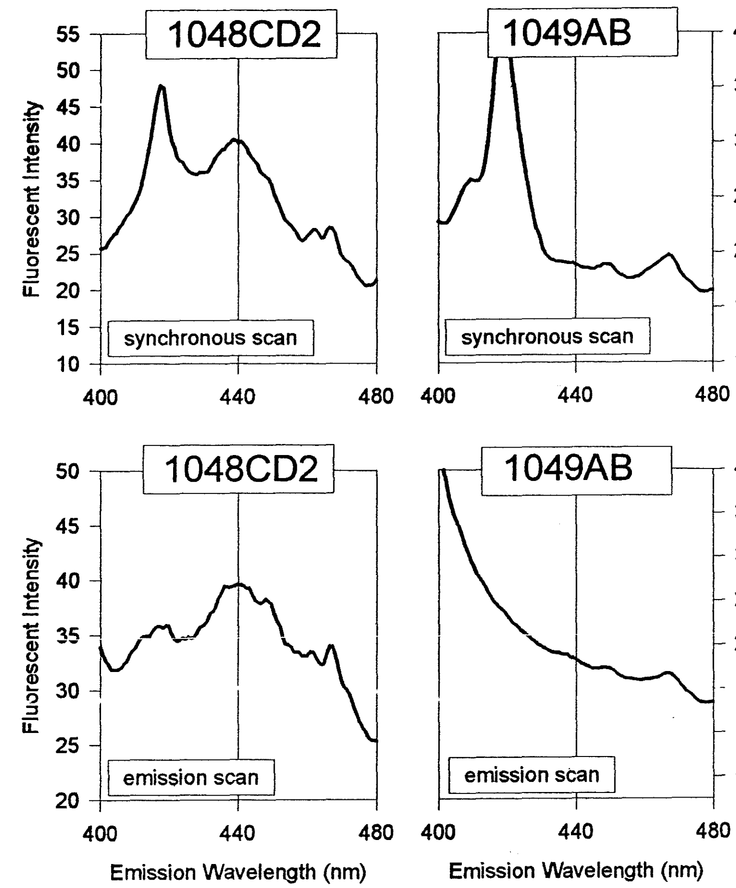

# Miesville

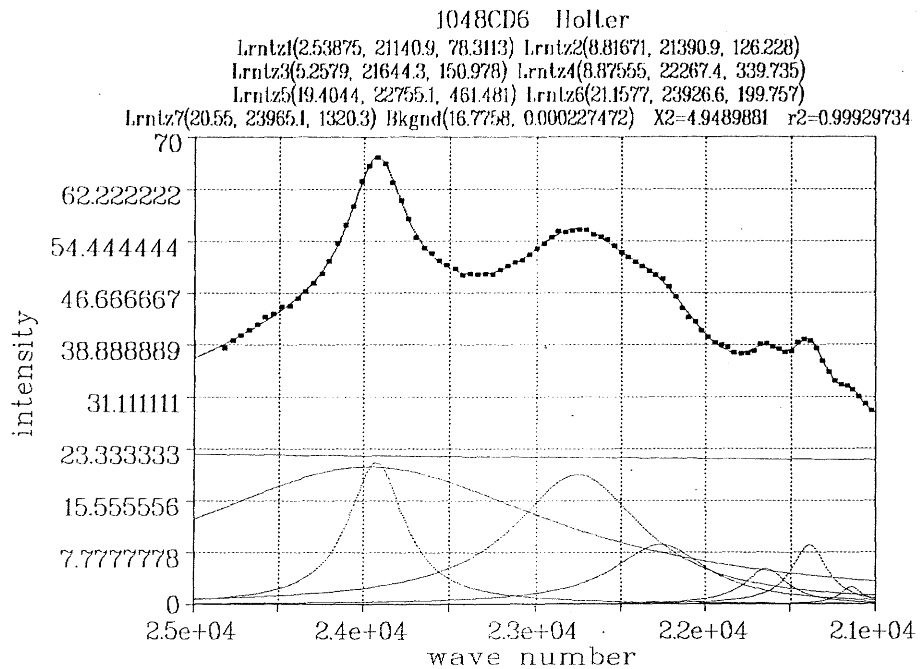


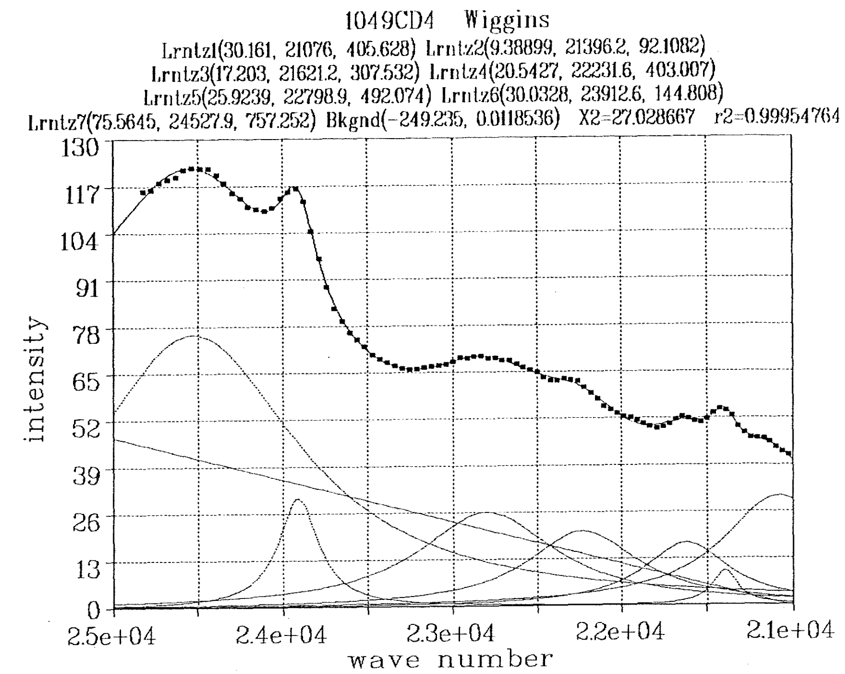
# Nininger




# Rosemount






1048CD6 Holter                                  Dec 14,1994 6:21 PM
92 Active X-Y Points
X: wave number          Mean: 22822.24163   SD: 1113.1365918
Y: intensity            Mean: 46.864380435  SD: 8.7976315954
File Source: 1048CD6.PRN
Curve-Fit Std Error= 0.267814237     r2= 0.999297343

Background Coefficients [y=a+bx+cx^2+dx^3]

| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | 16.775831 | 0.0002275 | | |

Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 2.5387472 | 2.114e+04 | 78.311344 | | |
| 2 | Lorentzian | 8.8167053 | 2.139e+04 | 126.22761 | | |
| 3 | Lorentzian | 5.2579028 | 2.164e+04 | 150.97849 | | |
| 4 | Lorentzian | 8.8755518 | 2.227e+04 | 339.73505 | | |
| 5 | Lorentzian | 19.404357 | 2.276e+04 | 461.48059 | | |
| 6 | Lorentzian | 21.157736 | 2.393e+04 | 199.75712 | | |
| 7 | Lorentzian | 20.550031 | 2.397e+04 | 1320.298 | | |

Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 2.5387472 | 2.114e+04 | 156.62052 | 501.27885 | 0.517512 |
| 2 | Lorentzian | 8.8167053 | 2.139e+04 | 252.45425 | 3084.6369 | 3.1845282 |
| 3 | Lorentzian | 5.2579028 | 2.164e+04 | 301.95665 | 2266.0791 | 2.3394626 |
| 4 | Lorentzian | 8.8755518 | 2.227e+04 | 679.46794 | 8269.3583 | 8.537149 |
| 5 | Loren[illegible]an | 19.404357 | 2.276e+04 | 922.9594 | 2.3[illegible]04 | 24.605111 |
| 6 | Lorer[illegible]n | 21.157736 | 2.393e+04 | 399.51142 | 1.2[illegible]04 | 12.45421 |

1049CD4 Wiggins                                 Dec 14,1994 6:45 PM
92 Active X-Y Points
X: wave number          Mean: 22822.24163   SD: 1113.1365918
Y: intensity            Mean: 73.717586957  SD: 25.624246955
File Source: 1049CD4.PRN
Curve-Fit Std Error= 0.625875241     r2= 0.999547643

Background Coefficients [y=a+bx+cx^2+dx^3]

| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | -249.2349 | 0.0118536 | | |

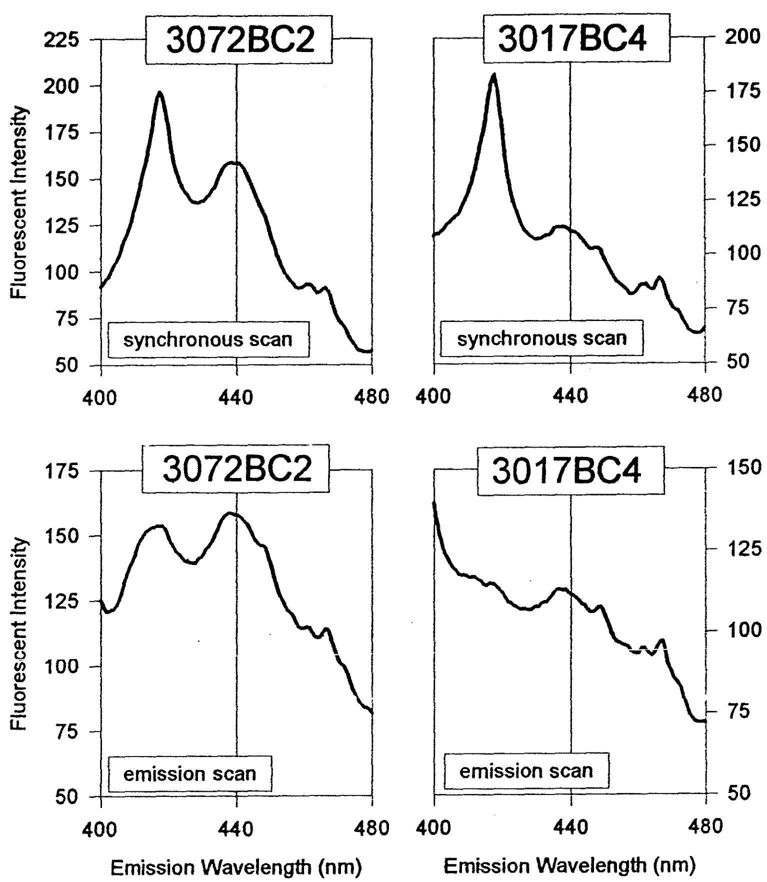
Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 30.160968 | 2.108e+04 | 405.62847 | | |
| 2 | Lorentzian | 9.3889906 | 2.14e+04 | 92.108239 | | |
| 3 | Lorentzian | 17.203027 | 2.162e+04 | 307.53245 | | |
| 4 | Lorentzian | 20.542656 | 2.223e+04 | 403.00713 | | |
| 5 | Lorentzian | 25.923905 | 2.28e+04 | 492.07405 | | |
| 6 | Lorentzian | 30.032812 | 2.391e+04 | 144.8084 | | |
| 7 | Lorentzian | 75.564497 | 2.453e+04 | 757.25152 | | |

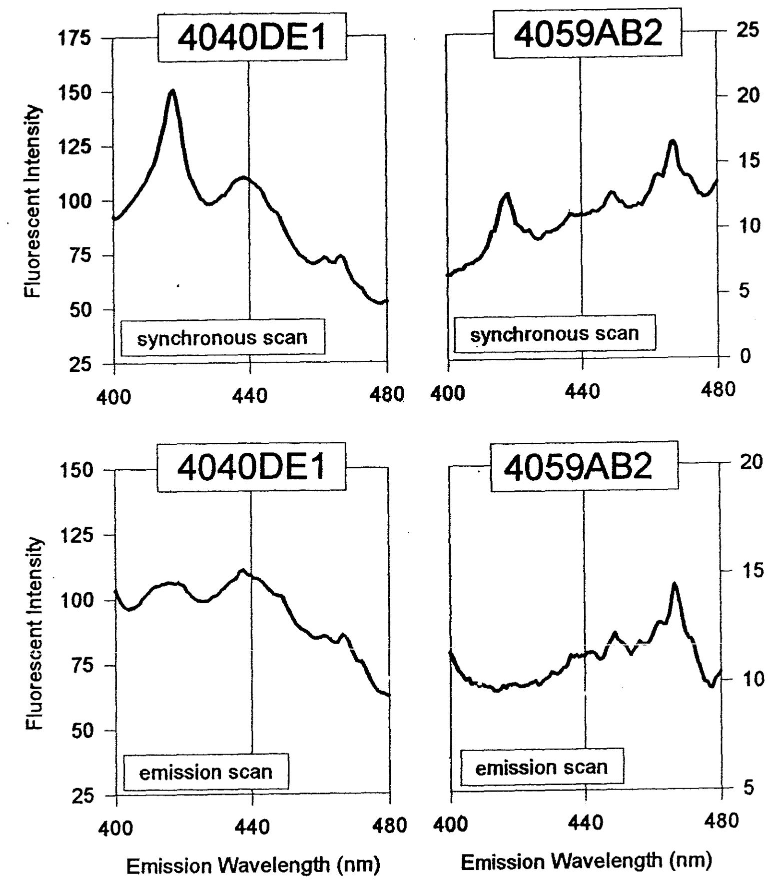
Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 30.160968 | 2.108e+04 | 811.25536 | 1.939e+04 | 9.5513489 |
| 2 | Lorentzian | 9.3889906 | 2.14e+04 | 184.2145 | 2482.6443 | 1.222665 |
| 3 | Lorentzian | 17.203027 | 2.162e+04 | 615.063 | 1.359e+04 | 6.6933124 |
| 4 | Lorentzian | 20.542656 | 2.223e+04 | 806.01332 | 2.206e+04 | 10.865212 |
| 5 | Loren[illegible]n | 25.923905 | 2.28e+04 | 984.1452 | 3.3[illegible]04 | 16.539731 |
| 6 | Lorer[illegible]n | 30.032812 | 2.391e+04 | 289.61464 | 1.[illegible]04 | 6.2846926 |

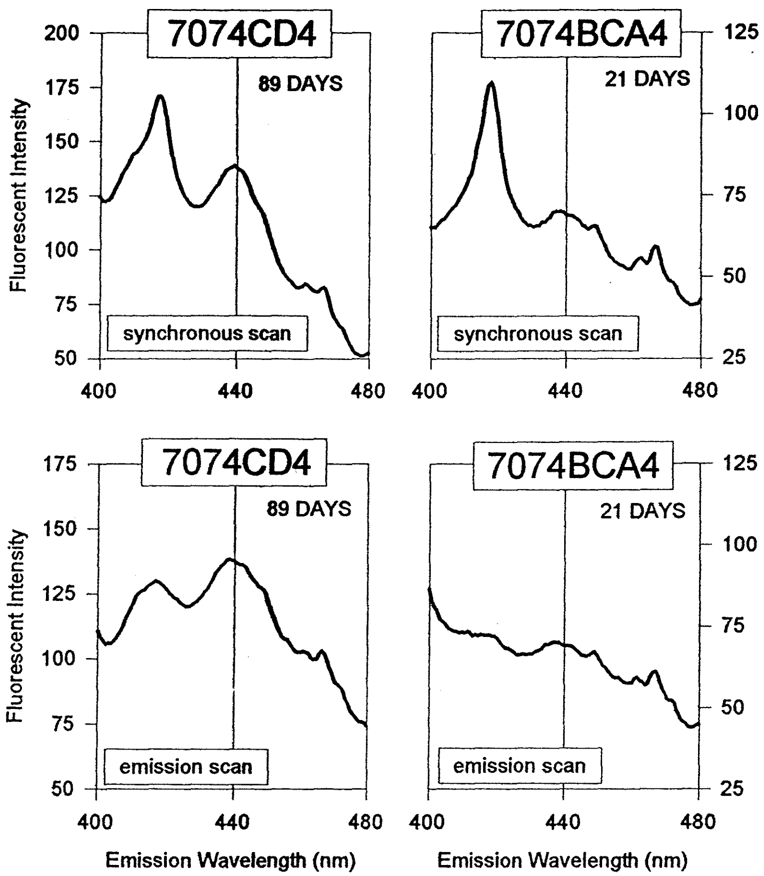
# Fairview



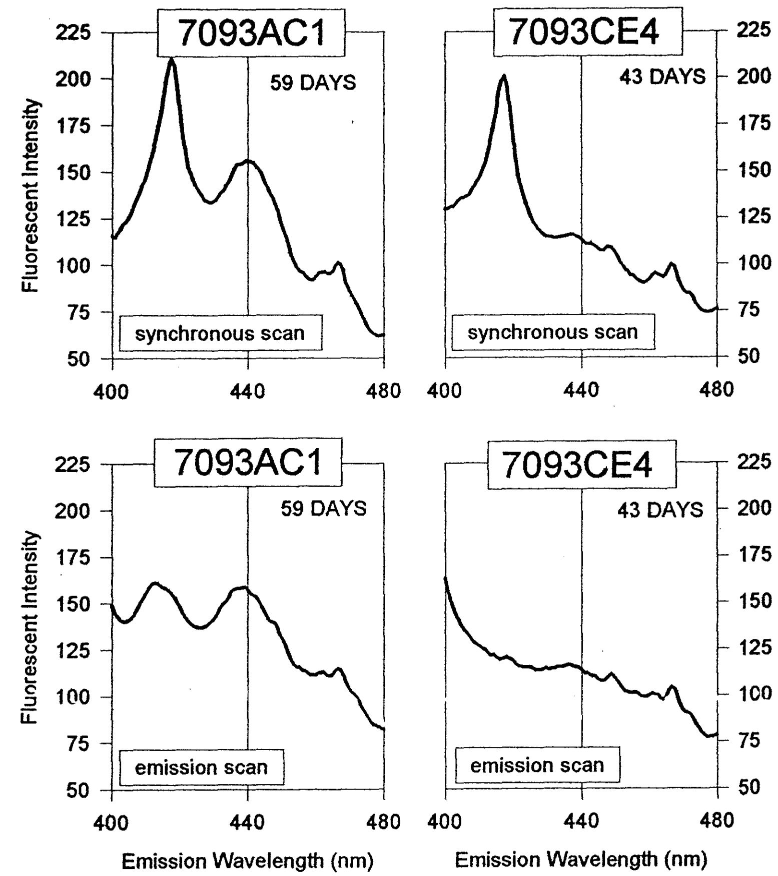

# Vasa

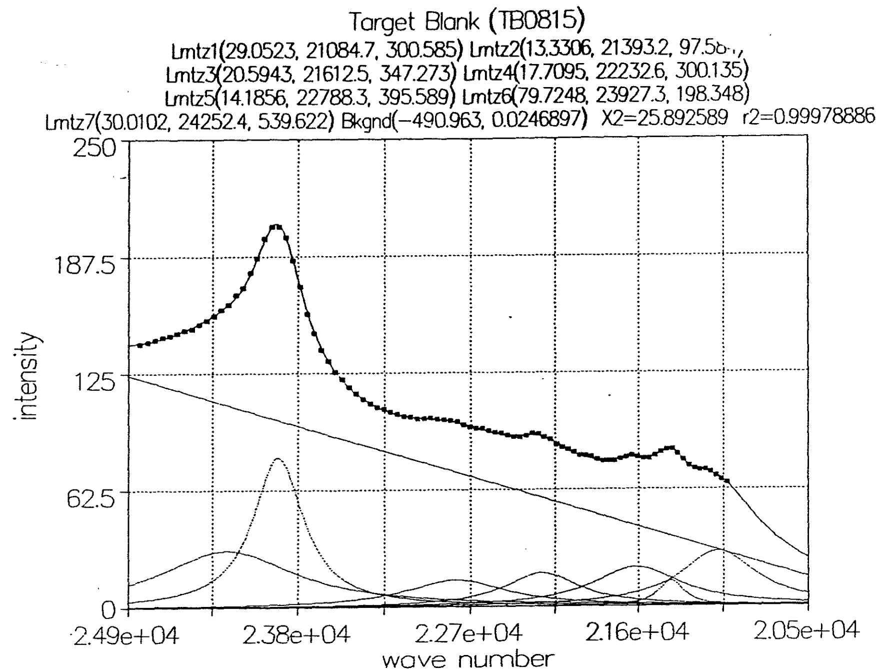


# Pleasant Grove




# Marion






Target Blank (TB0815) Oct 6,1994 5:51 PM
92 Active X-Y Points
X: wave number Mean: 22822.24163 SD: 1113.1365918
Y: intensity Mean: 110.76328261 SD: 36.709913467
File Source: TB08152.PRN
Curve-Fit Std Error= 0.612580541 r2= 0.999788862

Background Coefficients [y=a+bx+cx^2+dx^3]

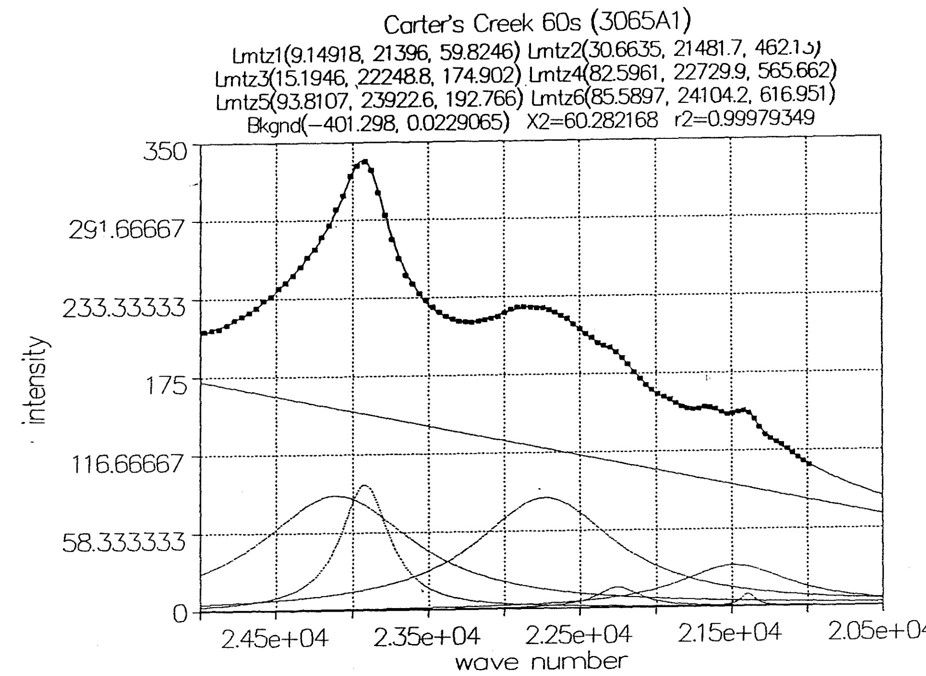
| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | -490.9634 | 0.0246897 | | |

Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 29.052348 | 2.108e+04 | 300.58508 | | |
| 2 | Lorentzian | 13.330638 | 2.139e+04 | 97.584037 | | |
| 3 | Lorentzian | 20.594266 | 2.161e+04 | 347.27333 | | |
| 4 | Lorentzian | 17.709499 | 2.223e+04 | 300.13503 | | |
| 5 | Lorentzian | 14.185602 | 2.279e+04 | 395.58935 | | |
| 6 | Lorentzian | 79.724785 | 2.393e+04 | 198.34823 | | |
| 7 | Lorentzian | 30.010232 | 2.425e+04 | 539.62248 | | |

Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area | |
|---|---|---|---|---|---|---|---|
| 1 | Lorentzian | 29.052348 | 2.108e+04 | 601.16731 | 1.47e+04 | 9.9624505 | |
| 2 | Lorentzian | 13.330638 | 2.139e+04 | 195.16712 | 3711.7781 | 2.5160709 | |
| 3 | Lorentzian | 20.594266 | 2.161e+04 | 694.54572 | 1.787e+04 | 12.11629 | |
| 4 | Lorentzian | 17.709499 | 2.223e+04 | 600.26915 | 1.479e+04 | 10.025561 | |
| 5 | Lorentzian | 14.185602 | 2.279e+04 | 791.17638 | 1.531e+04 | 10.381077 | * |
| 6 | Lorentzian | 79.724785 | 2.393e+04 | 396.69407 | 4.517e+04 | 30.615707 | |
| 7 | | | | | | 24.37 | * |




Carter's Creek 60s (3065A1) Oct 6,1994 5:39 PM
96 Active X-Y Points
X: wave number Mean: 22868.886354 SD: 1166.0763771
Y: intensity Mean: 204.81754167 SD: 55.432371607
File Source: 3065A1.PRN
Curve-Fit Std Error= 0.890610142 r2= 0.999793491

Background Coefficients [y=a+bx+cx^2+dx^3]

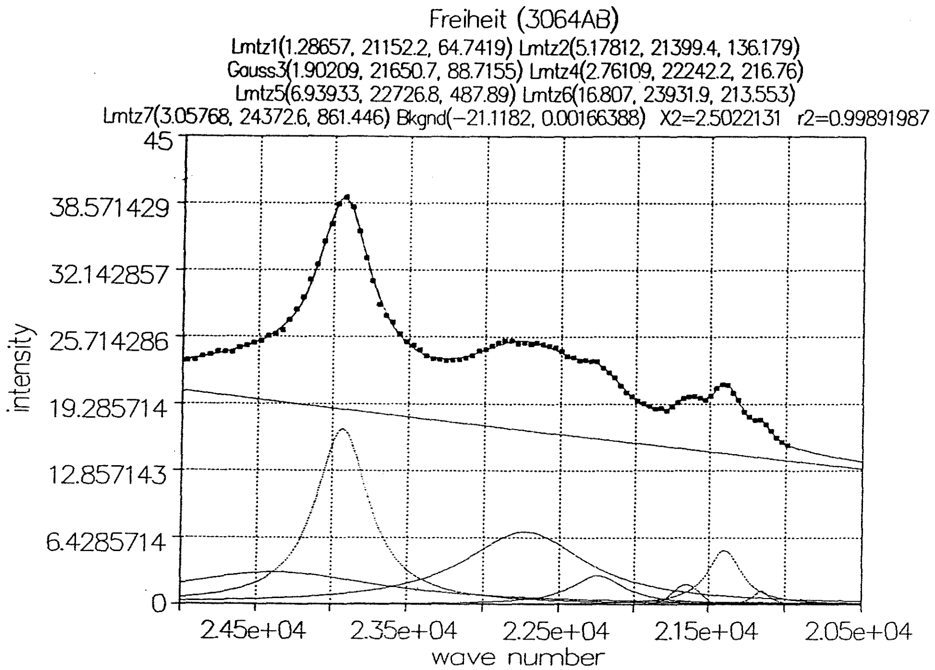
| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | -401.2982 | 0.0229065 | | |

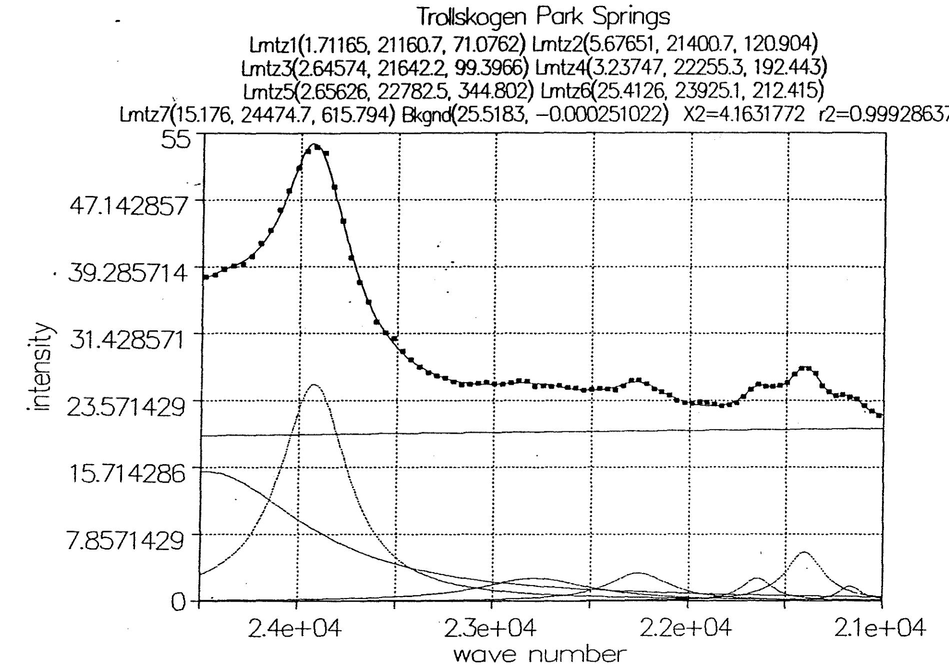
Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 9.1491837 | 2.14e+04 | 59.824588 | | |
| 2 | Lorentzian | 30.663454 | 2.148e+04 | 462.12978 | | |
| 3 | Lorentzian | 15.194639 | 2.225e+04 | 174.90226 | | |
| 4 | Lorentzian | 82.596143 | 2.273e+04 | 565.66223 | | |
| 5 | Lorentzian | 93.810675 | 2.392e+04 | 192.76597 | | |
| 6 | Lorentzian | 85.589659 | 2.41e+04 | 616.95114 | | |

Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area | |
|---|---|---|---|---|---|---|---|
| 1 | Lorentzian | 9.1491837 | 2.14e+04 | 119.64828 | 1630.1525 | 0.483279 | |
| 2 | Lorentzian | 30.663454 | 2.148e+04 | 924.2588 | 3.195e+04 | 9.4723998 | |
| 3 | Lorentzian | 15.194639 | 2.225e+04 | 349.8028 | 7811.6019 | 2.3158468 | |
| 4 | Lorentzian | 82.596143 | 2.273e+04 | 1131.3235 | 1.206e+05 | 35.740292 | * |
| 5 | Lorentzian | 93.810675 | 2.392e+04 | 385.52959 | 5.235e+04 | 15.519086 | |
| 6 | Lorentzian | 85.589659 | 2.41e+04 | 1233.9015 | 1.23e+05 | 36.469096 | * |
| | Total | | | | 3.373e+05 | 100 | |




Freiheit (3064AB) Oct 6,1994 8:42 PM
96 Active X-Y Points
X: wave number Mean: 22868.886354 SD: 1166.0763771
Y: intensity Mean: 23.937989583 SD: 4.9381390241
File Source: 3064AB2.PRN
Curve-Fit Std Error= 0.185140196 r2= 0.998919875

Background Coefficients [y=a+bx+cx^2+dx^3]

| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | -21.11825 | 0.0016639 | | |

Curve-Fit Coefficients

| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.2865701 | 2.115e+04 | 64.741937 | | |
| 2 | Lorentzian | 5.178121 | 2.14e+04 | 136.17898 | | |
| 3 | Gaussian | 1.9020876 | 2.165e+04 | 88.715548 | | |
| 4 | Lorentzian | 2.7610914 | 2.224e+04 | 216.75974 | | |
| 5 | Lorentzian | 6.9393321 | 2.273e+04 | 487.89005 | | |
| 6 | Lorentzian | 16.80701 | 2.393e+04 | 213.55283 | | |
| 7 | Lorentzian | 3.0576817 | 2.437e+04 | 861.44603 | | |

Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.2865701 | 2.115e+04 | 129.48172 | 228.48675 | 0.7959156 |
| 2 | Lorentzian | 5.178121 | 2.14e+04 | 272.35719 | 1961.5898 | 6.8330438 |
| 3 | Gaussian | 1.9020876 | 2.165e+04 | 208.90769 | 422.9803 | 1.4734186 |
| 4 | Lorentzian | 2.7610914 | 2.224e+04 | 433.51785 | 1730.1967 | 6.027004 |
| 5 | Lorentzian | 6.9393321 | 2.273e+04 | 975.77692 | 8985.[illegible]9 | 31.299226* |
| 6 | Lorent[illegible] | 16.80701 | 2.393e+04 | 427.10331 | 1.02[illegible] | 35.847199 |
| 7 | | | | | | 17.72 |

Trollskogen Park Springs Oct 6,1994 8:56 PM
85 Active X-Y Points
X: wave number Mean: 22669.282118 SD: 1015.075717
Y: intensity Mean: 29.411423529 SD: 8.3336802843
File Source: 5063AB2.PRN
Curve-Fit Std Error= 0.259129349 r2= 0.999286372

Background Coefficients [y=a+bx+cx^2+dx^3]

| Background | a | b | c | d |
|---|---|---|---|---|
| Order= 1 | 25.518329 | -0.000251 | | |

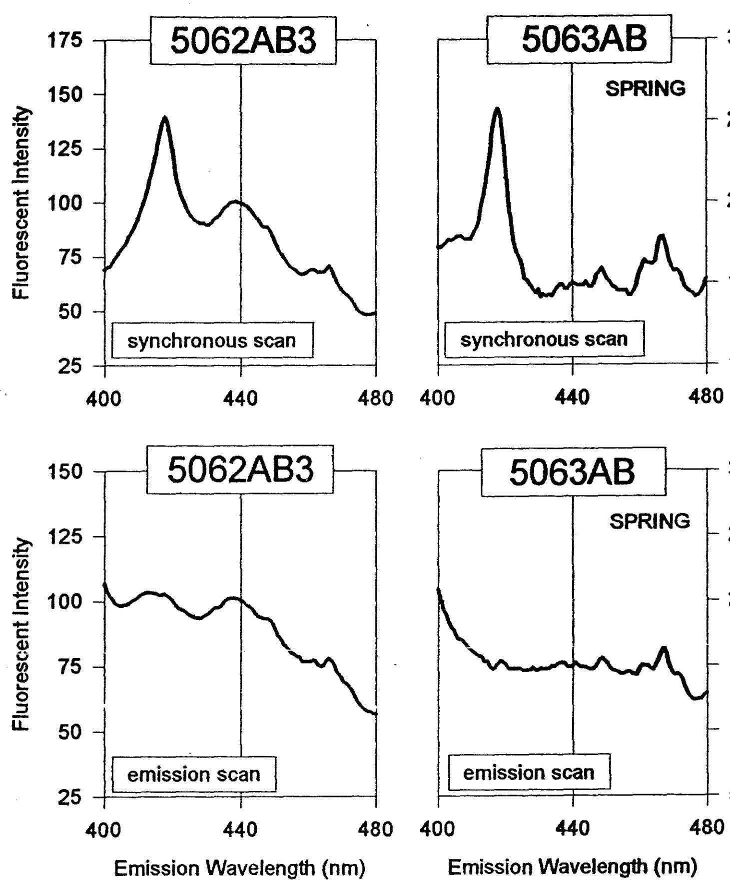
Curve-Fit Coefficients

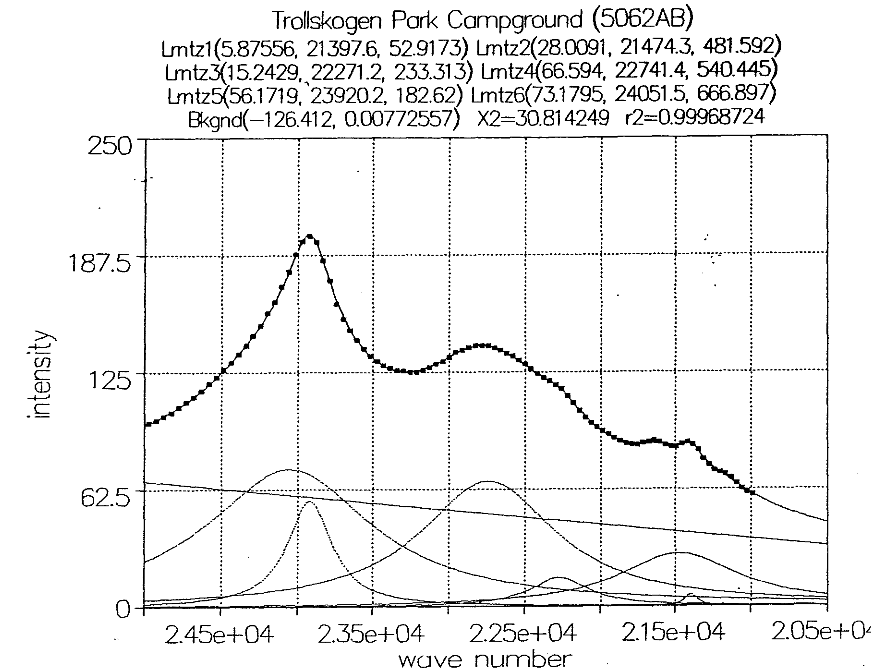
| Peak# | Type | Ampl | Ctr | Wid1 | Wid2 | Wid3 |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.7116493 | 2.116e+04 | 71.076203 | | |
| 2 | Lorentzian | 5.676511 | 2.14e+04 | 120.90358 | | |
| 3 | Lorentzian | 2.6457414 | 2.164e+04 | 99.396644 | | |
| 4 | Lorentzian | 3.2374714 | 2.226e+04 | 192.44301 | | |
| 5 | Lorentzian | 2.6562585 | 2.278e+04 | 344.80208 | | |
| 6 | Lorentzian | 25.412568 | 2.393e+04 | 212.41501 | | |
| 7 | Lorentzian | 15.175984 | 2.447e+04 | 615.79421 | | |

Measured Values

| Peak# | Type | PkAmpl | PkCtr | Wid@HM | Area | %Area |
|---|---|---|---|---|---|---|
| 1 | Lorentzian | 1.7116493 | 2.116e+04 | 142.15052 | 320.47564 | 0.911992 |
| 2 | Lorentzian | 5.676511 | 2.14e+04 | 241.80577 | 1914.9436 | 5.4494416 |
| 3 | Lorentzian | 2.6457414 | 2.164e+04 | 198.79173 | 774.91251 | 2.2052035 |
| 4 | Lorentzian | 3.2374714 | 2.226e+04 | 384.88463 | 1806.9236 | 5.1420441 |
| 5 | Lorentzian | 2.6562585 | 2.278e+04* | 689.60207 | 2516.[illegible]59 | 7.1623392* |
| 6 | Lorent[illegible] | 25.412568 | 2.393e+04 | 424.82862 | 1.46[illegible]4 | 41.573219 |
| 7 | | | | | | ~~35~~ 37.57 |

# Trollskogen




```
Trollskogen Park Campground (5062AB)          Oct 6,1994 5:45 PM
96 Active X-Y Points
X: wave number              Mean: 22868.886354   SD: 1166.0763771
Y: intensity                Mean: 118.10770833   SD: 32.203762784
File Source: 5062AB.PRN
Curve-Fit Std Error= 0.63675006       r2= 0.999687237

Background Coefficients [y=a+bx+cx^2+dx^3]
Background          a          b          c          d
    Order= 1    -126.4121  0.0077256

Curve-Fit Coefficients
Peak#  Type        Ampl        Ctr         Wid1        Wid2       Wid3
  1   Lorentzian  5.8755597   2.14e+04    52.917314
  2   Lorentzian  28.009147   2.147e+04   481.59203
  3   Lorentzian  15.242877   2.227e+04   233.31322
  4   Lorentzian  66.593987   2.274e+04   540.44526
  5   Lorentzian  56.171882   2.392e+04   182.61965
  6   Lorentzian  73.179542   2.405e+04   666.89726

Measured Values
Peak#  Type        PkAmpl      PkCtr       Wid@HM      Area       %Area
  1   Lorentzian  5.8755597   2.14e+04    105.83379   931.95616  0.3364154
  2   Lorentzian  28.009147   2.147e+04   963.18323   2.996e+04  10.816655
  3   Lorentzian  15.242877   2.227e+04   466.62565   1.023e+04  3.6911788
  4   Lorentzian  66.593987   2.274e+04   1080.8891   9.375e+04  33.840373*
  5   Lorentzian  56.171882   2.392e+04   365.23793   2.983e+04  10.767761
  6   Lorentzian  73.179542   2.405e+04   1333.7942   1.123e+05  40.547617
      Total                                          2.77e+05   100
```

| Location | Type | Samples | Mean OBI | (+/-) |
|---|---|---|---|---|
| 3044 | WWTP | 3 | 30.46 | + |
| 3020 | Creek | 2 | 16.09 | + |
| 3065 | Creek | 7 | 12.71 | + |
| 3066 | Creek | 5 | 2.52 | - |
| 1009 | Residential | 1 | 22.89 | + |
| 1046 | Residential | 2 | 11.42 | + |
| 1021 | Residential | 4 | 6.59 | + |
| 1039 | Residential | 6 | 5.08 | + |
| 7076 | Residential | 2 | 4.80 | + |
| 1083 | Residential | 2 | 4.70 | + |
| 1102 | Residential | 2 | 4.66 | + |
| 1082 | Residential | 2 | 4.50 | + |
| 1084 | Residential | 3 | 4.48 | + |
| 4041 | Residential | 2 | 4.29 | + |
| 3073 | Residential | 1 | 3.92 | + |
| 1089 | Residential | 2 | 3.86 | + |
| 1036 | Residential | 3 | 3.78 | + |
| 7077 | Residential | 1 | 3.77 | + |
| 7097 | Residential | 2 | 3.70 | + |
| 1052 | Residential | 2 | 3.69 | + |
| 1103 | Residential | 1 | 3.67 | + |
| 3072 | Residential | 2 | 3.65 | + |
| 3017 | Residential | 5 | 3.58 | + |
| 1090 | Residential | 1 | 3.55 | + |
| 4040 | Residential | 3 | 3.52 | + |
| 1014 | Residential | 1 | 3.50 | + |
| 1002 | Residential | 7 | 3.40 | + |
| 7074 | Residential | 3 | 3.34 | + |
| 1037 | Residential | 5 | 3.29 | + |
| 1088 | Residential | 2 | 3.23 | + |
| 1080 | Residential | 2 | 3.21 | + |
| 1069 | Residential | 3 | 3.05 | - |
| 7093 | Residential | 2 | 3.00 | - |
| 1028 | Residential | 6 | 3.00 | - |
| 9098 | Residential | 1 | 2.91 | - |
| 1034 | Residential | 4 | 2.91 | - |
| 1026 | Residential | 3 | 2.87 | - |
| 1051 | Residential | 3 | 2.84 | - |
| 1035 | Residential | 4 | 2.82 | - |
| 7075 | Residential | 2 | 2.81 | - |
| 1081 | Residential | 3 | 2.79 | - |
| 1029 | Residential | 3 | 2.76 | - |
| 7092 | Residential | 2 | 2.71 | - |
| 1005 | Residential | 1 | 2.61 | - |
| 1048 | Residential | 4 | 2.60 | - |
| 1038 | Residential | 4 | 2.60 | - |
| 1047 | Residential | 4 | 2.58 | - |
| 7094 | Residential | 1 | 2.58 | - |
| 1031 | Residential | 6 | 2.45 | - |





| | | | | |
|---|---|---|---|---|
| 1060 | Residential | 1 | 2.11 | - |
| 1003 | Residential | 7 | 2.09 | - |
| 7078 | Residential | 2 | 2.08 | - |
| 1008 | Residential | 1 | 2.06 | - |
| 1058 | Residential | 2 | 1.96 | - |
| 1030 | Residential | 4 | 1.86 | - |
| 3106 | Residential | 1 | 1.79 | - |
| 7095 | Residential | 2 | 1.75 | - |
| 1050 | Residential | 3 | 1.66 | - |
| 7096 | Residential | 2 | 1.56 | - |
| 3105 | Residential | 1 | 1.54 | - |
| 1049 | Residential | 4 | 1.51 | - |
| 1033 | Residential | 3 | 1.43 | - |
| 1013 | Residential | 1 | 1.33 | - |
| 4059 | Residential | 1 | 1.20 | - |
| 1016 | Residential | 1 | 0.98 | - |
| 1024 | Public | 1 | 4.69 | + |
| 5062 | Public | 1 | 4.21 | + |
| 4045 | Public | 3 | 3.76 | + |
| 1079 | Public | 2 | 3.01 | - |
| 1087 | Public | 2 | 1.80 | - |
| 3061 | Spring | 1 | 3.34 | + |
| 1006 | Spring | 7 | 2.64 | - |
| 3056 | Spring | 4 | 2.41 | - |
| 8054 | Spring | 4 | 2.40 | - |
| 3064 | Spring | 2 | 2.15 | - |
| 8053 | Spring | 4 | 2.12 | - |
| 1007 | Spring | 4 | 1.92 | - |
| 3057 | Spring | 3 | 1.80 | - |
| 3043 | Spring | 1 | 1.79 | - |
| 3019 | Spring | 2 | 1.49 | - |
| 3018 | Spring | 2 | 1.45 | - |
| 5063 | Spring | 1 | 1.03 | - |

| | | | | P/N cutoff | | |
|---|---|---|---|---|---|---|
| | | | | 3.20 | 89.25 | % of scans, OBI same as visual |
| | | | | | | |
| Loc. | Event | OBI | visual determination | OBI determination | OBI same as visual? | Filename |
| 0 | BB | 3.10 | N | N | 1 | B:\BATCH4\0000BB.FWA |
| 1002 | BD | 4.50 | P | P | 1 | B:\BATCH4\1002BD.FWA |
| 1002 | CD | 1.00 | N | N | 1 | B:\BATCH4\1002CD.FWA |
| 1002 | CD | 1.00 | N | N | 1 | B:\BATCH4\1002CD1.FWA |
| 1002 | CD | 0.86 | N | N | 1 | B:\BATCH4\1002CD2.FWA |
| 1002 | EF | 2.35 | N | N | 1 | B:\BATCH13\1002EF.FWA |
| 1002 | EF | 3.64 | P | P | 1 | B:\BATCH13\1002EF2.FWA |
| 1002 | EF | 1.34 | N | N | 1 | B:\BATCH13\1002EF3.FWA |
| 1002 | EF | 4.85 | P | P | 1 | B:\BATCH13\1002EF4.FWA |
| 1002 | EF | 3.65 | P | P | 1 | B:\BATCH13\1002EF5.FWA |
| 1002 | FG | 2.23 | N | N | 1 | B:\BATCH20\1002FG.FWA |
| 1002 | FG | 2.41 | N | N | 1 | B:\BATCH20\1002FG2.FWA |
| 1002 | FG | 1.51 | N | N | 1 | B:\BATCH20\1002FG3.FWA |
| 1002 | FG | 1.92 | N | N | 1 | B:\BATCH20\1002FG4.FWA |
| 1002 | FG | 3.43 | P | P | 1 | B:\BATCH20\1002FG5.FWA |
| 1002 | FG | 2.96 | I | N | 0 | B:\BATCH20\1002FG6.FWA |
| 1002 | GH | 2.89 | I | N | 0 | B:\BATCH29\1002GH1.FWA |
| 1002 | GH | 3.44 | I | P | 0 | B:\BATCH29\1002GH2.FWA |
| 1002 | GH | 3.65 | P | P | 1 | B:\BATCH29\1002GH3.FWA |
| 1002 | GH | 3.39 | I | P | 0 | B:\BATCH29\1002GH4.FWA |
| 1002 | GH | 1.86 | N | N | 1 | B:\BATCH29\1002GH5.FWA |
| 1002 | HI | 7.75 | P | P | 1 | B:\BATCH33\1002HI1.FWA |
| 1002 | HI | 8.60 | P | P | 1 | B:\BATCH33\1002HI2.FWA |
| 1002 | HI | 7.09 | P | P | 1 | B:\BATCH33\1002HI3.FWA |
| 1002 | IJ | 2.14 | N | N | 1 | A:\BATCH41\1002IJ1.FWA |
| 1002 | IJ | 1.67 | N | N | 1 | A:\BATCH41\1002IJ2.FWA |
| 1003 | BD | 0.92 | N | N | 1 | B:\BATCH9\1003BD.FWA |
| 1003 | BD | 0.84 | N | N | 1 | B:\BATCH9\1003BD1.FWA |
| 1003 | CD | 1.86 | N | N | 1 | B:\BATCH9\1003CD1.FWA |
| 1003 | CD | 1.43 | N | N | 1 | B:\BATCH9\1003CD2.FWA |
| 1003 | CD | 1.14 | N | N | 1 | B:\BATCH9\1003CD3.FWA |
| 1003 | DE | 1.22 | N | N | 1 | B:\BATCH13\1003DE.FWA |
| 1003 | DE | 1.06 | N | N | 1 | B:\BATCH13\1003DE2.FWA |
| 1003 | DE | 2.26 | N | N | 1 | B:\BATCH13\1003DE3.FWA |
| 1003 | DE | 2.01 | N | N | 1 | B:\BATCH13\1003DE4.FWA |
| 1003 | DE | 2.05 | N | N | 1 | B:\BATCH13\1003DE5.FWA |
| 1003 | FG | 2.33 | I | N | 0 | B:\BATCH29\1003FG1.FWA |
| 1003 | FG | 1.86 | I | N | 0 | B:\BATCH29\1003FG2.FWA |
| 1003 | FG | 1.48 | N | N | 1 | B:\BATCH29\1003FG3.FWA |
| 1003 | FG | 1.52 | N | N | 1 | B:\BATCH29\1003FG4.FWA |
| 1003 | FG | 1.59 | N | N | 1 | B:\BATCH29\1003FG5.FWA |
| 1003 | GH | 3.09 | I | N | 0 | B:\BATCH31\1003GH1.FWA |
| 1003 | GH | 4.07 | P | P | 1 | B:\BATCH31\1003GH2.FWA |
| 1003 | GH | 3.45 | P | P | 1 | B:\BATCH31\1003GH3.FWA |
| 1003 | GH | 6.25 | P | P | 1 | B:\BATCH31\1003GH4.FWA |
| 1003 | GH | 2.73 | I | N | 0 | B:\BATCH31\1003GH5.FWA |





| | | | | | | |
|---|---|---|---|---|---|---|
| 1003 | GH | 2.42 | N | N | 1 | B:\BATCH31\1003GH6.FWA |
| 1003 | HI | 3.78 | P | P | 1 | B:\BATCH34\1003HI1.FWA |
| 1003 | HI | 2.37 | N | N | 1 | B:\BATCH34\1003HI2.FWA |
| 1003 | HI | 3.45 | P | P | 1 | B:\BATCH34\1003HI3.FWA |
| 1003 | HI | 2.91 | I | N | 0 | B:\BATCH34\1003HI4.FWA |
| 1003 | IJ | 2.07 | N | N | 1 | A:\BATCH41\1003IJ1.FWA |
| 1003 | IJ | 1.97 | N | N | 1 | A:\BATCH41\1003IJ2.FWA |
| 1005 | CD | 3.18 | I | N | 0 | B:\BATCH35\1005CD1.FWA |
| 1005 | CD | 2.03 | N | N | 1 | B:\BATCH35\1005CD2.FWA |
| 1006 | AC | 3.29 | I | P | 0 | B:\BATCH3\1006AC.FWA |
| 1006 | AC | 2.06 | N | N | 1 | B:\BATCH3\1006AC2.FWA |
| 1006 | BC | 3.13 | N | N | 1 | B:\BATCH3\1006BC.FWA |
| 1006 | BC | 3.81 | I | P | 0 | B:\BATCH3\1006BC2.FWA |
| 1006 | BD | 1.28 | N | N | 1 | B:\BATCH5\1006BD.FWA |
| 1006 | BD | 1.36 | N | N | 1 | B:\BATCH5\1006BD1.FWA |
| 1006 | EF | 1.44 | N | N | 1 | B:\BATCH17\1006EF.FWA |
| 1006 | EF | 1.48 | N | N | 1 | B:\BATCH17\1006EF2.FWA |
| 1006 | EF | 1.97 | N | N | 1 | B:\BATCH17\1006EF3.FWA |
| 1006 | EF | 1.78 | N | N | 1 | B:\BATCH17\1006EF4.FWA |
| 1006 | FG | 2.46 | N | N | 1 | B:\BATCH25\1006FG1.FWA |
| 1006 | FG | 4.60 | P | P | 1 | B:\BATCH25\1006FG2.FWA |
| 1006 | FG | 3.71 | P | P | 1 | B:\BATCH25\1006FG3.FWA |
| 1006 | GH | 2.15 | N | N | 1 | B:\BATCH34\1006GH1.FWA |
| 1006 | HI | 3.94 | P | P | 1 | A:\BATCH42\1006HI1.FWA |
| 1006 | HI | 3.22 | N | P | 0 | A:\BATCH42\1006HI2.FWA |
| 1007 | BC | 0.94 | N | N | 1 | B:\BATCH5\1007BC.FWA |
| 1007 | CD | 2.47 | N | N | 1 | B:\BATCH13\1007CD.FWA |
| 1007 | DE | 2.49 | N | N | 1 | B:\BATCH17\1007DE.FWA |
| 1007 | DE | 1.62 | N | N | 1 | B:\BATCH17\1007DE2.FWA |
| 1007 | FG | 3.46 | P | P | 1 | B:\BATCH34\1007FG1.FWA |
| 1007 | FG | 1.71 | N | N | 1 | B:\BATCH34\1007FG3.FWA |
| 1007 | FG | 1.79 | N | N | 1 | B:\BATCH34\1007FG4.FWA |
| 1007 | FG | 1.92 | N | N | 1 | B:\BATCH34\1007FG5.FWA |
| 1008 | BC | 2.06 | N | N | 1 | B:\BATCH6\1008BC.FWA |
| 1009 | BC | 8.29 | P | P | 1 | B:\BATCH14\1009BC.FWA |
| 1009 | BC | 37.49 | P | P | 1 | B:\BATCH14\1009BC2.FWA |
| 1013 | BC | 1.41 | N | N | 1 | B:\BATCH6\1013BC.FWA |
| 1013 | BC | 1.32 | N | N | 1 | B:\BATCH6\1013BC1.FWA |
| 1013 | BC | 1.25 | N | N | 1 | B:\BATCH6\1013BC2.FWA |
| 1014 | BC | 3.50 | I | P | 0 | B:\BATCH6\1014BC.FWA |
| 1016 | AC | 0.98 | N | N | 1 | B:\BATCH9\1016AC.FWA |
| 1021 | AB | 3.67 | P | P | 1 | B:\BATCH6\1021AB.FWA |
| 1021 | CD | 14.26 | P | P | 1 | B:\BATCH14\1021CD.FWA |
| 1021 | CD | 9.01 | P | P | 1 | B:\BATCH14\1021CD2.FWA |
| 1021 | CD | 3.39 | P | P | 1 | B:\BATCH14\1021CD3.FWA |
| 1021 | EF | 4.60 | P | P | 1 | B:\BATCH21\1021EF.FWA |
| 1021 | EF | 3.21 | P | P | 1 | B:\BATCH21\1021EF2.FWA |
| 1021 | EF | 3.66 | P | P | 1 | B:\BATCH21\1021EF3.FWA |
| 1021 | EF | 4.38 | P | P | 1 | B:\BATCH21\1021EF4.FWA |
| 1021 | EF | 19.17 | P | P | 1 | B:\BATCH21\1021EF5.FWA |
| 1021 | EF | 11.63 | P | P | 1 | B:\BATCH21\1021EF6.FWA |

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| 1021 | EF | 21.95 | P | P | 1 | B:\BATCH21\1021EF7.FWA |
| 1021 | EF | 21.02 | P | P | 1 | B:\BATCH21\1021EF8.FWA |
| 1021 | FG | 1.86 | N | N | 1 | a:\batch39\1021FG1.FWA |
| 1021 | FG | 2.98 | I | N | 0 | a:\batch39\1021FG2.FWA |
| 1021 | FG | 3.40 | I | P | 0 | a:\batch39\1021FG3.FWA |
| 1021 | FG | 2.10 | N | N | 1 | a:\batch39\1021FG4.FWA |
| 1024 | AB | 3.89 | I | P | 0 | B:\BATCH3\1024AB.FWA |
| 1024 | AB | 5.48 | P | P | 1 | B:\BATCH3\1024AB2.FWA |
| 1026 | AB | 2.44 | N | N | 1 | B:\BATCH9\1026AB.FWA |
| 1026 | CD | 1.33 | N | N | 1 | B:\BATCH24\1026CD1.FWA |
| 1026 | CD | 3.60 | I | P | 0 | B:\BATCH24\1026CD2.FWA |
| 1026 | CD | 1.53 | N | N | 1 | B:\BATCH24\1026CD3.FWA |
| 1026 | CD | 3.18 | I | N | 0 | B:\BATCH24\1026CD4.FWA |
| 1026 | CD | 1.31 | N | N | 1 | B:\BATCH24\1026CD5.FWA |
| 1026 | DE | 5.57 | P | P | 1 | a:\batch39\1026DE1.FWA |
| 1026 | DE | 1.46 | N | N | 1 | a:\batch39\1026DE2.FWA |
| 1026 | DE | 6.25 | P | P | 1 | a:\batch39\1026DE3.FWA |
| 1026 | DE | 2.60 | N | N | 1 | a:\batch39\1026DE4.FWA |
| 1028 | AC | 2.10 | N | N | 1 | B:\BATCH4\1028AC.FWA |
| 1028 | BC | 2.69 | N | N | 1 | B:\BATCH4\1028BC1.FWA |
| 1028 | BC | 2.74 | N | N | 1 | B:\BATCH4\1028BC2.FWA |
| 1028 | BC | 2.76 | N | N | 1 | B:\BATCH4\1028BC3.FWA |
| 1028 | BC | 2.90 | N | N | 1 | B:\BATCH4\1028BC4.FWA |
| 1028 | DE | 1.53 | N | N | 1 | B:\BATCH13\1028DE.FWA |
| 1028 | EF | 3.72 | P | P | 1 | B:\BATCH20\1028EF.FWA |
| 1028 | EF | 4.90 | P | P | 1 | B:\BATCH20\1028EF2.FWA |
| 1028 | EF | 5.54 | P | P | 1 | B:\BATCH20\1028EF3.FWA |
| 1028 | EF | 3.97 | P | P | 1 | B:\BATCH20\1028EF4.FWA |
| 1028 | FG | 3.77 | P | P | 1 | B:\BATCH29\1028FG1.FWA |
| 1028 | FG | 3.92 | P | P | 1 | B:\BATCH29\1028FG2.FWA |
| 1028 | GH | 4.43 | P | P | 1 | B:\BATCH31\1028GH1.FWA |
| 1028 | GH | 2.67 | N | N | 1 | B:\BATCH31\1028GH2.FWA |
| 1028 | GH | 2.50 | N | N | 1 | B:\BATCH31\1028GH3.FWA |
| 1029 | AB | 1.61 | N | N | 1 | B:\BATCH13\1029AB.FWA |
| 1029 | AB | 1.96 | N | N | 1 | B:\BATCH13\1029AB2.FWA |
| 1029 | AB | 1.59 | N | N | 1 | B:\BATCH13\1029AB3.FWA |
| 1029 | BC | 2.99 | I | N | 0 | B:\BATCH17\1029BC.FWA Side A |
| 1029 | BC | 7.12 | P | P | 1 | B:\BATCH17\1029BC2.FWA Side B |
| 1029 | BC | 5.03 | P | P | 1 | B:\BATCH17\1029BC3.FWA Side B, rinsed |
| 1029 | BC | 4.76 | P | P | 1 | B:\BATCH17\1029BC4.FWA Side C |
| 1029 | BC | 2.94 | I | N | 0 | B:\BATCH17\1029BC5.FWA Side D |
| 1029 | CE | 2.09 | N | N | 1 | B:\BATCH28\1029CE1.FWA |
| 1029 | CE | 2.29 | N | N | 1 | B:\BATCH28\1029CE2.FWA |
| 1029 | CE | 1.82 | N | N | 1 | B:\BATCH28\1029CE3.FWA |
| 1029 | CE | 1.81 | N | N | 1 | B:\BATCH28\1029CE4.FWA |
| 1030 | AC | 1.72 | N | N | 1 | B:\BATCH11\1030AC1.FWA |
| 1030 | AC | 1.04 | N | N | 1 | B:\BATCH11\1030AC2.FWA |
| 1030 | AC | 1.06 | N | N | 1 | B:\BATCH11\1030AC3.FWA |
| 1030 | AC | 1.14 | N | N | 1 | B:\BATCH11\1030AC4.FWA |
| 1030 | AC | 0.91 | N | N | 1 | B:\BATCH11\1030AC5.FWA |
| 1030 | AC | 1.05 | N | N | 1 | B:\BATCH11\1030AC6.FWA |





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| 1030 | AC | 1.49 | N | N | 1 | B:\BATCH11\1030AC7.FWA |
| 1030 | DE | 1.79 | N | N | 1 | B:\BATCH19\1030DE.FWA |
| 1030 | DE | 1.77 | N | N | 1 | B:\BATCH19\1030DE2.FWA |
| 1030 | DE | 1.71 | N | N | 1 | B:\BATCH19\1030DE3.FWA |
| 1030 | DE | 1.77 | N | N | 1 | B:\BATCH19\1030DE4.FWA |
| 1030 | EF | 2.47 | I | N | 0 | B:\BATCH29\1030EF1.FWA |
| 1030 | EF | 3.62 | I | P | 0 | B:\BATCH29\1030EF2.FWA |
| 1030 | EF | 1.86 | N | N | 1 | B:\BATCH29\1030EF3.FWA |
| 1030 | EF | 2.15 | N | N | 1 | B:\BATCH29\1030EF4.FWA |
| 1030 | FG | 1.81 | N | N | 1 | B:\BATCH35\1030FG1.FWA |
| 1030 | FG | 1.34 | N | N | 1 | B:\BATCH35\1030FG2.FWA |
| 1030 | FG | 2.19 | N | N | 1 | B:\BATCH35\1030FG3.FWA |
| 1030 | FG | 2.44 | N | N | 1 | B:\BATCH35\1030FG4.FWA |
| 1031 | AC | 2.69 | N | N | 1 | B:\BATCH3\1031AC.FWA |
| 1031 | AC | 2.07 | N | N | 1 | B:\BATCH3\1031AC2.FWA |
| 1031 | AC | 2.02 | N | N | 1 | B:\BATCH3\1031AC3.FWA |
| 1031 | AE | 2.50 | N | N | 1 | B:\BATCH5\1031AE.FWA |
| 1031 | AE | 2.84 | I | N | 0 | B:\BATCH5\1031AE1.FWA |
| 1031 | AE | 2.78 | I | N | 0 | B:\BATCH5\1031AE2.FWA |
| 1031 | CE | 3.23 | I | P | 0 | B:\BATCH5\1031CE.FWA |
| 1031 | CE | 3.04 | I | N | 0 | B:\BATCH5\1031CE1.FWA |
| 1031 | EF | 1.71 | N | N | 1 | B:\BATCH4\1031EF.FWA |
| 1031 | EF | 1.79 | N | N | 1 | B:\BATCH4\1031EF1.FWA |
| 1031 | GH | 1.61 | N | N | 1 | B:\BATCH29\1031GH1.FWA |
| 1031 | GH | 1.81 | N | N | 1 | B:\BATCH29\1031GH2.FWA |
| 1031 | GH | 3.26 | P | P | 1 | B:\BATCH29\1031GH3.FWA |
| 1031 | GH | 5.80 | P | P | 1 | B:\BATCH29\1031GH4.FWA |
| 1031 | HI | 1.75 | N | N | 1 | B:\BATCH33\1031HI1.FWA |
| 1031 | HI | 1.85 | N | N | 1 | B:\BATCH33\1031HI2.FWA |
| 1031 | HI | 1.60 | N | N | 1 | B:\BATCH33\1031HI3.FWA |
| 1033 | AB | 1.18 | N | N | 1 | B:\BATCH6\1033AB.FWA |
| 1033 | CD | 0.63 | N | N | 1 | B:\BATCH14\1033CD.FWA |
| 1033 | CD | 2.70 | N | N | 1 | B:\BATCH14\1033CD2.FWA |
| 1033 | CD | 1.55 | N | N | 1 | B:\BATCH14\1033CD3.FWA |
| 1033 | CD | 1.16 | N | N | 1 | B:\BATCH14\1033CD4.FWA |
| 1033 | DE | 1.35 | N | N | 1 | B:\BATCH21\1033DE.FWA |
| 1033 | DE | 1.37 | N | N | 1 | B:\BATCH21\1033DE2.FWA |
| 1033 | DE | 2.27 | N | N | 1 | B:\BATCH21\1033DE3.FWA |
| 1033 | DE | 1.56 | N | N | 1 | B:\BATCH21\1033DE4.FWA |
| 1033 | DE | 1.44 | N | N | 1 | B:\BATCH21\1033DE5.FWA |
| 1034 | BD | 1.50 | N | N | 1 | B:\BATCH5\1034BD.FWA |
| 1034 | BD | 1.51 | N | N | 1 | B:\BATCH5\1034BD1.FWA |
| 1034 | EF | 2.60 | N | N | 1 | B:\BATCH17\1034EF.FWA |
| 1034 | EF | 1.95 | N | N | 1 | B:\BATCH17\1034EF2.FWA |
| 1034 | EF | 2.90 | N | N | 1 | B:\BATCH17\1034EF3.FWA |
| 1034 | EF | 3.31 | P | P | 1 | B:\BATCH17\1034EF4.FWA |
| 1034 | EF | 2.98 | N | N | 1 | B:\BATCH17\1034EF5.FWA |
| 1034 | EF | 3.04 | N | N | 1 | B:\BATCH17\1034EF6.FWA |
| 1034 | EF | 2.19 | N | N | 1 | B:\BATCH17\1034EF7.FWA |
| 1034 | FG | 1.80 | N | N | 1 | B:\BATCH29\1034FG1.FWA |
| 1034 | FG | 3.62 | P | P | 1 | B:\BATCH29\1034FG2.FWA |

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| 1034 | FG | 2.63 | N | N | 1 | B:\BATCH29\1034FG3.FWA |
| 1034 | FG | 2.35 | N | N | 1 | B:\BATCH29\1034FG4.FWA |
| 1034 | FG | 1.51 | N | N | 1 | B:\BATCH29\1034FG5.FWA |
| 1034 | FG | 3.32 | I | P | 0 | B:\BATCH29\1034FG6.FWA |
| 1034 | GH | 5.45 | P | P | 1 | B:\1034GH1.FWA |
| 1034 | GH | 5.42 | P | P | 1 | B:\1034GH2.FWA |
| 1034 | GH | 4.61 | P | P | 1 | B:\1034GH3.FWA |
| 1034 | GH | 4.00 | P | P | 1 | B:\1034GH4.FWA |
| 1035 | AB | 2.12 | N | N | 1 | B:\BATCH5\1035AB.FWA |
| 1035 | AB | 1.91 | N | N | 1 | B:\BATCH5\1035AB1.FWA |
| 1035 | CD | 3.27 | I | P | 0 | B:\BATCH13\1035CD.FWA |
| 1035 | CD | 2.86 | I | N | 0 | B:\BATCH13\1035CD2.FWA |
| 1035 | CD | 4.93 | P | P | 1 | B:\BATCH13\1035CD3.FWA |
| 1035 | CD | 3.17 | I | N | 0 | B:\BATCH13\1035CD4.FWA |
| 1035 | CD | 4.34 | P | P | 1 | B:\BATCH13\1035CD5.FWA |
| 1035 | DE | 4.85 | P | P | 1 | B:\BATCH24\1035DE1.FWA |
| 1035 | DE | 2.55 | N | N | 1 | B:\BATCH24\1035DE2.FWA |
| 1035 | DE | 1.66 | N | N | 1 | B:\BATCH24\1035DE3.FWA |
| 1035 | DE | 2.02 | N | N | 1 | B:\BATCH24\1035DE4.FWA |
| 1035 | DE | 2.63 | N | N | 1 | B:\BATCH24\1035DE5.FWA |
| 1035 | DE | 2.22 | N | N | 1 | B:\BATCH24\1035DE6.FWA |
| 1035 | DE | 1.41 | N | N | 1 | B:\BATCH24\1035DE7.FWA |
| 1035 | EF | 2.51 | N | N | 1 | B:\BATCH31\1035EF1.FWA |
| 1035 | EF | 3.91 | P | P | 1 | B:\BATCH31\1035EF2.FWA |
| 1035 | EF | 2.21 | N | N | 1 | B:\BATCH31\1035EF3.FWA |
| 1035 | EF | 3.66 | P | P | 1 | B:\BATCH31\1035EF4.FWA |
| 1036 | AB | 2.26 | N | N | 1 | B:\BATCH6\1036AB.FWA |
| 1036 | CD | 5.31 | P | P | 1 | B:\BATCH20\1036CD.FWA |
| 1036 | CD | 4.79 | P | P | 1 | B:\BATCH20\1036CD2.FWA |
| 1036 | CD | 6.34 | P | P | 1 | B:\BATCH20\1036CD3.FWA |
| 1036 | CD | 4.75 | P | P | 1 | B:\BATCH20\1036CD4.FWA |
| 1036 | DE | 3.04 | N | N | 1 | B:\BATCH29\1036DE1.FWA |
| 1036 | DE | 2.07 | N | N | 1 | B:\BATCH29\1036DE2.FWA |
| 1036 | DE | 4.09 | P | P | 1 | B:\BATCH29\1036DE3.FWA |
| 1036 | DE | 3.26 | I | P | 0 | B:\BATCH29\1036DE4.FWA |
| 1036 | DE | 6.57 | P | P | 1 | B:\BATCH29\1036DE5.FWA |
| 1036 | DE | 3.72 | P | P | 1 | B:\BATCH29\1036DE6.FWA |
| 1037 | AD | 2.61 | N | N | 1 | B:\BATCH13\1037AD.FWA |
| 1037 | AD | 2.94 | I | N | 0 | B:\BATCH13\1037AD2.FWA |
| 1037 | AD | 2.34 | N | N | 1 | B:\BATCH13\1037AD3.FWA |
| 1037 | BC | 1.72 | N | N | 1 | B:\BATCH8\1037BC1.FWA |
| 1037 | BC | 1.97 | N | N | 1 | B:\BATCH8\1037BC2.FWA |
| 1037 | BC | 1.60 | N | N | 1 | B:\BATCH8\1037BC3.FWA |
| 1037 | DE | 3.98 | P | P | 1 | B:\BATCH18\1037DE.FWA |
| 1037 | DE | 3.96 | P | P | 1 | B:\BATCH18\1037DE2.FWA |
| 1037 | DE | 3.14 | I | N | 0 | B:\BATCH18\1037DE3.FWA |
| 1037 | EF | 4.74 | P | P | 1 | B:\BATCH30\1037EF1.FWA |
| 1037 | EF | 2.97 | N | N | 1 | B:\BATCH30\1037EF2.FWA |
| 1037 | EF | 2.89 | N | N | 1 | B:\BATCH30\1037EF3.FWA |
| 1037 | EF | 4.08 | P | P | 1 | B:\BATCH30\1037EF4.FWA |
| 1037 | FG | 3.94 | I | P | 0 | B:\BATCH38\1037FG1.FWA |





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| 1037 | FG | 6.22 | P | P | 1 | B:\BATCH38\1037FG2.FWA |
| 1037 | FG | 4.07 | P | P | 1 | B:\BATCH38\1037FG3.FWA |
| 1037 | FG | 4.51 | P | P | 1 | B:\BATCH38\1037FG4.FWA |
| 1038 | AB | 2.16 | N | N | 1 | B:\BATCH8\1038AB1.FWA |
| 1038 | CD | 2.99 | N | N | 1 | B:\BATCH19\1038CD.FWA |
| 1038 | CD | 3.05 | N | N | 1 | B:\BATCH19\1038CD2.FWA |
| 1038 | CD | 3.04 | N | N | 1 | B:\BATCH19\1038CD3.FWA |
| 1038 | CD | 2.84 | N | N | 1 | B:\BATCH19\1038CD5.FWA |
| 1038 | DE | 1.98 | N | N | 1 | B:\BATCH29\1038DE.FWA |
| 1038 | DE | 2.69 | I | N | 0 | B:\BATCH29\1038DE2.FWA |
| 1038 | DE | 2.05 | N | N | 1 | B:\BATCH29\1038DE3.FWA |
| 1038 | DE | 2.13 | N | N | 1 | B:\BATCH29\1038DE4.FWA |
| 1038 | EF | 2.81 | I | N | 0 | B:\BATCH33\1038EF1.FWA |
| 1038 | EF | 3.55 | I | P | 0 | B:\BATCH33\1038EF2.FWA |
| 1038 | EF | 2.74 | N | N | 1 | B:\BATCH33\1038EF3.FWA |
| 1039 | AB | 8.53 | P | P | 1 | B:\BATCH7\1039AB.FWA |
| 1039 | AC | 5.32 | P | P | 1 | B:\BATCH13\1039AC.FWA |
| 1039 | AC | 3.94 | P | P | 1 | B:\BATCH13\1039AC2.FWA |
| 1039 | AC | 2.34 | N | N | 1 | B:\BATCH13\1039AC3.FWA |
| 1039 | AC | 3.21 | I | P | 0 | B:\BATCH13\1039AC4.FWA |
| 1039 | CD | 4.68 | P | P | 1 | B:\BATCH15\1039CD.FWA |
| 1039 | CD | 2.16 | N | N | 1 | B:\BATCH15\1039CD2.FWA |
| 1039 | CD | 1.73 | N | N | 1 | B:\BATCH15\1039CD3.FWA |
| 1039 | CD | 1.67 | N | N | 1 | B:\BATCH15\1039CD4.FWA |
| 1039 | DE | 6.35 | P | P | 1 | B:\BATCH20\1039DE.FWA |
| 1039 | DE | 6.02 | P | P | 1 | B:\BATCH20\1039DE2.FWA |
| 1039 | DE | 5.26 | P | P | 1 | B:\BATCH20\1039DE3.FWA |
| 1039 | DE | 7.36 | P | P | 1 | B:\BATCH20\1039DE4.FWA |
| 1039 | EF | 4.95 | P | P | 1 | B:\BATCH29\1039EF1.FWA |
| 1039 | EF | 3.19 | N | N | 1 | B:\BATCH29\1039EF2.FWA |
| 1039 | EF | 3.58 | P | P | 1 | B:\BATCH29\1039EF3.FWA |
| 1039 | EF | 1.77 | N | N | 1 | B:\BATCH29\1039EF4.FWA |
| 1039 | EF | 9.96 | P | P | 1 | B:\BATCH29\1039EF5.FWA |
| 1039 | FG | 6.39 | P | P | 1 | B:\BATCH36\1039FG1.FWA |
| 1039 | FG | 6.39 | P | P | 1 | B:\BATCH36\1039FG1.FWA |
| 1039 | FG | 2.32 | N | N | 1 | B:\BATCH36\1039FG2.FWA |
| 1039 | FG | 3.56 | I | P | 0 | B:\BATCH36\1039FG3.FWA |
| 1039 | FG | 5.02 | P | P | 1 | B:\BATCH36\1039FG4.FWA |
| 1046 | BC | 2.59 | N | N | 1 | a:\batch39\1046BC2.FWA |
| 1046 | BC | 2.73 | N | N | 1 | a:\batch39\1046BC.FWA |
| 1046 | BC | 2.48 | N | N | 1 | a:\batch39\1046BC4.FWA |
| 1046 | BC | 26.67 | P | P | 1 | a:\batch39\1046BC5.FWA |
| 1046 | BC | 7.66 | P | P | 1 | a:\batch39\1046BC6.FWA |
| 1046 | CD | 14.41 | P | P | 1 | a:\batch39\1046CD1.FWA |
| 1047 | AB | 0.97 | N | N | 1 | B:\BATCH10\1047AB.FWA |
| 1047 | AB | 0.95 | N | N | 1 | B:\BATCH10\1047AB1.FWA |
| 1047 | AC | 2.60 | N | N | 1 | B:\BATCH14\1047AC.FWA |
| 1047 | AC | 4.43 | P | P | 1 | B:\BATCH14\1047AC2.FWA |
| 1047 | AC | 3.26 | N | P | 0 | B:\BATCH14\1047AC3.FWA |
| 1047 | AC | 5.22 | P | P | 1 | B:\BATCH14\1047AC4.FWA |
| 1047 | CD | 2.73 | N | N | 1 | B:\BATCH24\1047CD1.FWA |

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|---|---|---|---|---|---|---|
| 1047 | CD | 2.78 | I | N | 0 | B:\BATCH24\1047CD2.FWA |
| 1047 | CD | 3.25 | I | P | 0 | B:\BATCH24\1047CD3.FWA |
| 1047 | CD | 3.26 | P | P | 1 | B:\BATCH24\1047CD4.FWA |
| 1047 | CD | 2.69 | I | N | 0 | B:\BATCH24\1047CD5.FWA |
| 1047 | CD | 2.27 | N | N | 1 | B:\BATCH24\1047CD6.FWA |
| 1047 | DE | 2.78 | N | N | 1 | B:\BATCH38\1047DE1.FWA |
| 1047 | DE | 3.49 | I | P | 0 | B:\BATCH38\1047DE2.FWA |
| 1047 | DE | 1.77 | N | N | 1 | B:\BATCH38\1047DE3.FWA |
| 1047 | DE | 2.62 | N | N | 1 | B:\BATCH38\1047DE4.FWA |
| 1048 | AB | 1.24 | N | N | 1 | B:\BATCH10\1048AB.FWA |
| 1048 | AB | 1.20 | N | N | 1 | B:\BATCH10\1048AB1.FWA |
| 1048 | AC | 1.33 | N | N | 1 | B:\BATCH13\1048AC.FWA |
| 1048 | AC | 4.34 | P | P | 1 | B:\BATCH13\1048AC2.FWA |
| 1048 | AC | 4.14 | P | P | 1 | B:\BATCH13\1048AC3.FWA |
| 1048 | AC | 1.55 | N | N | 1 | B:\BATCH13\1048AC4.FWA |
| 1048 | CD | 5.39 | P | P | 1 | B:\BATCH19\1048CD.FWA |
| 1048 | CD | 5.31 | P | P | 1 | B:\BATCH19\1048CD2.FWA |
| 1048 | CD | 3.59 | P | P | 1 | B:\BATCH19\1048CD4.FWA |
| 1048 | CD | 5.24 | P | P | 1 | B:\BATCH19\1048CD5.FWA |
| 1048 | CD | 5.24 | P | P | 1 | B:\BATCH19\1048CD6.FWA |
| 1048 | DE | 0.84 | N | N | 1 | a:\batch39\1048DE1.FWA |
| 1048 | DE | 1.69 | N | N | 1 | a:\batch39\1048DE2.FWA |
| 1048 | DE | 1.31 | N | N | 1 | a:\batch39\1048DE3.FWA |
| 1048 | DE | 1.58 | N | N | 1 | a:\batch39\1048DE4.FWA |
| 1048 | DE | 1.78 | N | N | 1 | a:\batch39\1048DE5.FWA |
| 1048 | DE | 1.21 | N | N | 1 | a:\batch39\1048DE6.FWA |
| 1049 | AB | -0.70 | N | N | 1 | B:\BATCH10\1049AB.FWA |
| 1049 | AC | 1.26 | N | N | 1 | B:\BATCH13\1049AC.FWA |
| 1049 | AC | 1.90 | N | N | 1 | B:\BATCH13\1049AC2.FWA |
| 1049 | CD | 2.12 | N | N | 1 | B:\BATCH18\1049CD.FWA |
| 1049 | CD | 2.66 | N | N | 1 | B:\BATCH18\1049CD2.FWA |
| 1049 | CD | 4.06 | P | P | 1 | B:\BATCH18\1049CD3.FWA |
| 1049 | CD | 3.48 | P | P | 1 | B:\BATCH18\1049CD4.FWA |
| 1049 | CD | 4.49 | P | P | 1 | B:\BATCH18\1049CD5.FWA |
| 1049 | CD | 1.57 | N | N | 1 | B:\BATCH18\1049CD6.FWA |
| 1049 | DE | 2.19 | N | N | 1 | a:\batch39\1049DE1.FWA |
| 1049 | DE | 1.23 | N | N | 1 | a:\batch39\1049DE2.FWA |
| 1049 | DE | 1.61 | N | N | 1 | a:\batch39\1049DE3.FWA |
| 1049 | DE | 1.72 | N | N | 1 | a:\batch39\1049DE4.FWA |
| 1049 | DE | 2.11 | N | N | 1 | a:\batch39\1049DE5.FWA |
| 1049 | DE | 3.76 | N | P | 0 | a:\batch39\1049DE6.FWA |
| 1050 | AB | 1.59 | N | N | 1 | B:\BATCH10\1050AB1.FWA |
| 1050 | AB | 1.04 | N | N | 1 | B:\BATCH10\1050AB2.FWA |
| 1050 | AC | 1.35 | N | N | 1 | B:\BATCH13\1050AC.FWA |
| 1050 | AC | 1.27 | N | N | 1 | B:\BATCH13\1050AC2.FWA |
| 1050 | AC | 1.61 | N | N | 1 | B:\BATCH13\1050AC3.FWA |
| 1050 | AC | 1.36 | N | N | 1 | B:\BATCH13\1050AC5.FWA |
| 1050 | CD | 1.79 | N | N | 1 | B:\BATCH17\1050CD.FWA |
| 1050 | CD | 2.50 | N | N | 1 | B:\BATCH17\1050CD2.FWA |
| 1050 | CD | 1.58 | N | N | 1 | B:\BATCH17\1050CD3.FWA |
| 1050 | CD | 2.45 | N | N | 1 | B:\BATCH17\1050CD4.FWA |





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| 1050 | CD | 2.33 | N | N | 1 | B:\BATCH17\1050CD5.FWA |
| 1050 | CD | 2.93 | N | N | 1 | B:\BATCH17\1050CD6.FWA |
| 1051 | AB | 3.59 | N | P | 0 | B:\BATCH14\1051AB.FWA |
| 1051 | AB | 2.31 | N | N | 1 | B:\BATCH14\1051AB2.FWA |
| 1051 | AB | 2.43 | N | N | 1 | B:\BATCH14\1051AB3.FWA |
| 1051 | BC | 2.75 | N | N | 1 | B:\BATCH20\1051BC.FWA |
| 1051 | BC | 1.61 | N | N | 1 | B:\BATCH20\1051BC3.FWA |
| 1051 | CD | 3.40 | I | P | 0 | a:\batch39\1051CD.FWA |
| 1051 | CD | 4.45 | I | P | 0 | a:\batch39\1051CD2.FWA |
| 1051 | CD | 1.83 | N | N | 1 | a:\batch39\1051CD3.FWA |
| 1051 | CD | 4.52 | I | P | 0 | a:\batch39\1051CD4.FWA |
| 1052 | AB | 5.29 | I | P | 0 | B:\BATCH13\1052AB.FWA |
| 1052 | AB | 1.52 | I | N | 0 | B:\BATCH13\1052AB2.FWA |
| 1052 | BC | 3.78 | P | P | 1 | B:\BATCH20\1052BC.FWA |
| 1052 | BC | 3.40 | P | P | 1 | B:\BATCH20\1052BC2.FWA |
| 1052 | BC | 3.45 | I | P | 0 | B:\BATCH20\1052BC3.FWA |
| 1052 | BC | 5.29 | P | P | 1 | B:\BATCH20\1052BC4.FWA |
| 1058 | AB | 1.84 | N | N | 1 | B:\BATCH21\1058AB.FWA |
| 1058 | AB | 1.79 | N | N | 1 | B:\BATCH21\1058AB2.FWA |
| 1058 | AB | 1.50 | N | N | 1 | B:\BATCH21\1058ABD.FWA |
| 1058 | C | 2.20 | N | N | 1 | B:\BATCH21\1058C.FWA |
| 1060 | AB | 1.95 | N | N | 1 | B:\BATCH21\1060AB.FWA |
| 1060 | AB | 2.48 | N | N | 1 | B:\BATCH21\1060AB3.FWA |
| 1060 | AB | 1.78 | N | N | 1 | B:\BATCH21\1060AB4.FWA |
| 1060 | AB | 2.22 | N | N | 1 | B:\BATCH21\1060AB5.FWA |
| 1069 | AB | 2.21 | N | N | 1 | B:\BATCH24\1069AB1.FWA |
| 1069 | AB | 1.72 | N | N | 1 | B:\BATCH24\1069AB2.FWA |
| 1069 | AB | 4.01 | P | P | 1 | B:\BATCH24\1069AB3.FWA |
| 1069 | AB | 3.60 | P | P | 1 | B:\BATCH24\1069AB4.FWA |
| 1069 | AB | 3.47 | P | P | 1 | B:\BATCH24\1069AB5.FWA |
| 1069 | BD | 3.46 | I | P | 0 | B:\BATCH38\1069BD1.FWA |
| 1069 | BD | 2.26 | N | N | 1 | B:\BATCH38\1069BD2.FWA |
| 1069 | BD | 5.43 | P | P | 1 | B:\BATCH38\1069BD3.FWA |
| 1069 | BD | 5.40 | P | P | 1 | B:\BATCH38\1069BD4.FWA |
| 1069 | CD | 3.13 | N | N | 1 | B:\BATCH38\1069CD1.FWA |
| 1069 | CD | 1.48 | N | N | 1 | B:\BATCH38\1069CD2.FWA |
| 1069 | CD | 1.89 | N | N | 1 | B:\BATCH38\1069CD3.FWA |
| 1069 | CD | 1.56 | N | N | 1 | B:\BATCH38\1069CD4.FWA |
| 1079 | BC | 5.19 | P | P | 1 | B:\BATCH34\1079BC1.FWA |
| 1079 | BC | 4.18 | P | P | 1 | B:\BATCH34\1079BC2.FWA |
| 1079 | BC | 3.22 | I | P | 0 | B:\BATCH34\1079BC3.FWA |
| 1079 | BC | 4.79 | P | P | 1 | B:\BATCH34\1079BC4.FWA |
| 1079 | BC | 2.74 | N | N | 1 | B:\BATCH34\1079BC5.FWA |
| 1079 | CD | 1.69 | N | N | 1 | A:\BATCH41\1079CD1.FWA |
| 1079 | CD | 2.31 | N | N | 1 | A:\BATCH41\1079CD2.FWA |
| 1080 | AB | 1.41 | N | N | 1 | B:\BATCH24\1080AB1.FWA |
| 1080 | AB | 2.70 | N | N | 1 | B:\BATCH24\1080AB2.FWA |
| 1080 | AB | 5.51 | P | P | 1 | B:\BATCH24\1080AB3.FWA |
| 1080 | AB | 4.71 | P | P | 1 | B:\BATCH24\1080AB4.FWA |
| 1080 | AB | 4.16 | P | P | 1 | B:\BATCH24\1080AB5.FWA |
| 1080 | AB | 1.63 | N | N | 1 | B:\BATCH24\1080AB7.FWA |

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|---|---|---|---|---|---|---|
| 1080 | CD | 2.36 | N | N | 1 | B:\BATCH35\1080CD1.FWA |
| 1080 | CD | 3.36 | I | P | 0 | B:\BATCH35\1080CD2.FWA |
| 1080 | CD | 3.13 | N | N | 1 | B:\BATCH35\1080CD3.FWA |
| 1080 | CD | 3.42 | I | P | 0 | B:\BATCH35\1080CD4.FWA |
| 1081 | AB | 4.83 | P | P | 1 | B:\BATCH24\1081AB1.FWA |
| 1081 | AB | 7.30 | P | P | 1 | B:\BATCH24\1081AB2.FWA |
| 1081 | AB | 4.18 | P | P | 1 | B:\BATCH24\1081AB3.FWA |
| 1081 | AB | 3.87 | P | P | 1 | B:\BATCH24\1081AB4.FWA |
| 1081 | AB | 4.05 | P | P | 1 | B:\BATCH24\1081AB5.FWA |
| 1081 | AB | 1.99 | N | N | 1 | B:\BATCH24\1081AB6.FWA |
| 1081 | AB | 3.34 | P | P | 1 | B:\BATCH24\1081AB7.FWA |
| 1081 | AB | 3.33 | P | P | 1 | B:\BATCH24\1081AB8.FWA |
| 1081 | AC | 2.86 | I | N | 0 | B:\BATCH28\1081AC1.FWA |
| 1081 | AC | 2.42 | N | N | 1 | B:\BATCH28\1081AC2.FWA |
| 1081 | AC | 1.89 | N | N | 1 | B:\BATCH28\1081AC3.FWA |
| 1081 | AC | 1.81 | N | N | 1 | B:\BATCH28\1081AC4.FWA |
| 1081 | BC | 1.74 | N | N | 1 | B:\BATCH28\1081BC1.FWA |
| 1081 | BC | 2.29 | N | N | 1 | B:\BATCH28\1081BC2.FWA |
| 1082 | AB | 4.45 | P | P | 1 | B:\BATCH27\1082AB1.FWA |
| 1082 | AB | 4.85 | P | P | 1 | B:\BATCH27\1082AB2.FWA |
| 1082 | AB | 4.39 | P | P | 1 | B:\BATCH27\1082AB3.FWA |
| 1082 | AB | 5.56 | P | P | 1 | B:\BATCH27\1082AB4.FWA |
| 1082 | BC | 3.45 | N | P | 0 | A:\BATCH41\1082BC1.FWA |
| 1082 | BC | 3.64 | I | P | 0 | A:\BATCH41\1082BC2.FWA |
| 1082 | BC | 3.38 | N | P | 0 | A:\BATCH41\1082BC3.FWA |
| 1082 | BC | 7.50 | P | P | 1 | A:\BATCH41\1082BC4.FWA |
| 1082 | BC | 3.18 | N | N | 1 | A:\BATCH41\1082BC5.FWA |
| 1082 | BC | 3.93 | N | P | 0 | A:\BATCH41\1082BC6.FWA |
| 1083 | AB | 3.60 | P | P | 1 | B:\BATCH27\1083AB1.FWA |
| 1083 | AB | 3.39 | P | P | 1 | B:\BATCH27\1083AB2.FWA |
| 1083 | AB | 4.10 | P | P | 1 | B:\BATCH27\1083AB3.FWA |
| 1083 | AB | 3.79 | P | P | 1 | B:\BATCH27\1083AB4.FWA |
| 1083 | BD | 3.81 | N | P | 0 | A:\BATCH41\1083BD1.FWA |
| 1083 | BD | 7.85 | P | P | 1 | A:\BATCH41\1083BD2.FWA |
| 1083 | BD | 3.06 | N | N | 1 | A:\BATCH41\1083BD3.FWA |
| 1083 | BD | 9.50 | P | P | 1 | A:\BATCH41\1083BD4.FWA |
| 1083 | BD | 5.52 | P | P | 1 | A:\BATCH41\1083BD5.FWA |
| 1083 | BD | 4.35 | P | P | 1 | A:\BATCH41\1083BD6.FWA |
| 1084 | AB | 2.02 | N | N | 1 | B:\BATCH26\1084AB1.FWA |
| 1084 | AB | 2.06 | N | N | 1 | B:\BATCH26\1084AB2.FWA |
| 1084 | AB | 4.57 | P | P | 1 | B:\BATCH26\1084AB3.FWA |
| 1084 | AB | 3.99 | P | P | 1 | B:\BATCH26\1084AB4.FWA |
| 1084 | AB | 2.54 | N | N | 1 | B:\BATCH26\1084AB5.FWA |
| 1084 | AC | 3.80 | P | P | 1 | B:\BATCH29\1084AC1.FWA |
| 1084 | AC | 3.50 | P | P | 1 | B:\BATCH29\1084AC2.FWA |
| 1084 | AC | 3.04 | P | N | 0 | B:\BATCH29\1084AC3.FWA |
| 1084 | BD | 6.97 | P | P | 1 | B:\BATCH35\1084BD.FWA |
| 1087 | AB | 1.40 | N | N | 1 | B:\1087AB1.FWA |
| 1087 | AB | 1.20 | N | N | 1 | B:\1087AB2.FWA |
| 1087 | AB | 0.98 | N | N | 1 | B:\1087AB3.FWA |
| 1087 | AB | 1.40 | N | N | 1 | B:\1087AB4.FWA |





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| 1087 | AB | 1.04 | N | N | 1 | B:\1087AB5.FWA |
| 1087 | BC | 2.72 | N | N | 1 | A:\BATCH42\1087BC1.FWA |
| 1087 | BC | 2.06 | N | N | 1 | A:\BATCH42\1087BC2.FWA |
| 1088 | AB | 2.85 | N | N | 1 | B:\BATCH29\1088AB1.FWA |
| 1088 | AB | 4.36 | P | P | 1 | B:\BATCH29\1088AB2.FWA |
| 1088 | AB | 3.82 | P | P | 1 | B:\BATCH29\1088AB3.FWA |
| 1088 | AB | 4.91 | P | P | 1 | B:\BATCH29\1088AB4.FWA |
| 1088 | AB | 6.44 | P | P | 1 | B:\BATCH29\1088AB5.FWA |
| 1088 | AB | 1.79 | N | N | 1 | B:\BATCH29\1088AB6.FWA |
| 1088 | BC | 1.29 | N | N | 1 | A:\BATCH41\1088BC1.FWA |
| 1088 | BC | 2.05 | N | N | 1 | A:\BATCH41\1088BC2.FWA |
| 1088 | BC | 2.59 | N | N | 1 | A:\BATCH41\1088BC3.FWA |
| 1088 | BC | 4.74 | P | P | 1 | A:\BATCH41\1088BC4.FWA |
| 1088 | BC | 2.46 | N | N | 1 | A:\BATCH41\1088BC5.FWA |
| 1088 | BC | 1.51 | N | N | 1 | A:\BATCH41\1088BC6.FWA |
| 1089 | AB | 3.53 | I | P | 0 | B:\BATCH33\1089AB1.FWA |
| 1089 | AB | 5.72 | P | P | 1 | B:\BATCH33\1089AB2.FWA |
| 1089 | AB | 3.43 | I | P | 0 | B:\BATCH33\1089AB3.FWA |
| 1089 | BC | 4.02 | I | P | 0 | A:\BATCH41\1089BC1.FWA |
| 1089 | BC | 2.97 | N | N | 1 | A:\BATCH41\1089BC2.FWA |
| 1090 | AD | 2.07 | N | N | 1 | B:\BATCH35\1090AD1.FWA |
| 1090 | AD | 5.54 | P | P | 1 | B:\BATCH35\1090AD2.FWA |
| 1090 | AD | 2.08 | N | N | 1 | B:\BATCH35\1090AD3.FWA |
| 1090 | AD | 4.50 | P | P | 1 | B:\BATCH35\1090AD4.FWA |
| 1102 | AB | 2.57 | N | N | 1 | B:\BATCH34\1102AB1.FWA |
| 1102 | AB | 2.03 | N | N | 1 | B:\BATCH34\1102AB2.FWA |
| 1102 | AB | 4.01 | P | P | 1 | B:\BATCH34\1102AB3.FWA |
| 1102 | AB | 4.12 | P | P | 1 | B:\BATCH34\1102AB4.FWA |
| 1102 | AB | 5.18 | P | P | 1 | B:\BATCH34\1102AB5.FWA |
| 1102 | BC | 8.67 | P | P | 1 | A:\BATCH42\1102BC1.FWA |
| 1102 | BC | 2.80 | N | N | 1 | A:\BATCH42\1102BC2.FWA |
| 1103 | AB | 4.89 | P | P | 1 | A:\BATCH42\1103AB1.FWA |
| 1103 | AB | 2.44 | N | N | 1 | A:\BATCH42\1103AB2.FWA |
| 3017 | BC | 4.70 | P | P | 1 | B:\BATCH25\3017BC1.FWA |
| 3017 | BC | 3.98 | P | P | 1 | B:\BATCH25\3017BC2.FWA |
| 3017 | BC | 4.13 | P | P | 1 | B:\BATCH25\3017BC3.FWA |
| 3017 | BC | 3.23 | P | P | 1 | B:\BATCH25\3017BC4.FWA |
| 3017 | BC | 2.74 | N | N | 1 | B:\BATCH25\3017BC5.FWA |
| 3017 | BC | 2.83 | I | N | 0 | B:\BATCH25\3017BC6.FWA |
| 3017 | BC | 2.90 | N | N | 1 | B:\BATCH25\3017BC7.FWA |
| 3017 | BD | 3.55 | P | P | 1 | B:\BATCH26\3017BD1.FWA |
| 3017 | BD | 4.14 | P | P | 1 | B:\BATCH26\3017BD2.FWA |
| 3017 | BD | 3.68 | P | P | 1 | B:\BATCH26\3017BD3.FWA |
| 3017 | BD | 5.09 | P | P | 1 | B:\BATCH26\3017BD4.FWA |
| 3017 | BE | 3.99 | P | P | 1 | B:\BATCH30\3017BE1.FWA |
| 3017 | BE | 3.90 | P | P | 1 | B:\BATCH30\3017BE2.FWA |
| 3017 | BE | 4.33 | P | P | 1 | B:\BATCH30\3017BE3.FWA |
| 3017 | BE | 3.31 | I | P | 0 | B:\BATCH30\3017BE4.FWA |
| 3017 | DF | 1.62 | N | N | 1 | A:\BATCH41\3017DF1.FWA |
| 3017 | DF | 5.03 | P | P | 1 | A:\BATCH41\3017DF2.FWA |
| 3017 | DF | 2.74 | N | N | 1 | A:\BATCH41\3017DF3.FWA |

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|---|---|---|---|---|---|---|
| 3017 | DF | 1.80 | N | N | 1 | A:\BATCH41\3017DF4.FWA |
| 3017 | EF | 3.93 | I | P | 0 | A:\BATCH41\3017EF1.FWA |
| 3017 | EF | 3.64 | I | P | 0 | A:\BATCH41\3017EF2.FWA |
| 3017 | EF | 2.67 | N | N | 1 | A:\BATCH41\3017EF3.FWA |
| 3017 | EF | 5.00 | P | P | 1 | A:\BATCH41\3017EF4.FWA |
| 3017 | EF | 2.83 | N | N | 1 | A:\BATCH41\3017EF5.FWA |
| 3018 | AB | 1.16 | N | N | 1 | B:\BATCH3\3018AB.FWA |
| 3018 | CD | 2.23 | N | N | 1 | B:\BATCH25\3018CD1.FWA |
| 3018 | CD | 1.24 | N | N | 1 | B:\BATCH25\3018CD2.FWA |
| 3019 | AB | 1.29 | N | N | 1 | B:\BATCH3\3019AB.FWA |
| 3019 | CD | 1.65 | N | N | 1 | B:\BATCH25\3019CD1.FWA |
| 3019 | CD | 2.17 | N | N | 1 | B:\BATCH25\3019CD2.FWA |
| 3019 | CD | 1.27 | N | N | 1 | B:\BATCH25\3019CD3.FWA |
| 3019 | CD | 1.65 | N | N | 1 | B:\BATCH25\3019CD4.FWA |
| 3020 | AB | 9.81 | P | P | 1 | B:\BATCH3\3020AB.FWA |
| 3020 | AB | 8.05 | P | P | 1 | B:\BATCH3\3020AB3.FWA |
| 3020 | CD | 23.24 | P | P | 1 | B:\BATCH15\3020CD.FWA |
| 3043 | CD | 2.22 | N | N | 1 | B:\BATCH30\3043CD1.FWA |
| 3043 | CD | 2.24 | N | N | 1 | B:\BATCH30\3043CD2.FWA |
| 3043 | CD | 0.71 | I | N | 0 | B:\BATCH30\3043CD3.FWA |
| 3043 | CD | 1.97 | N | N | 1 | B:\BATCH30\3043CD4.FWA |
| 3044 | BC | 34.87 | P | P | 1 | B:\BATCH11\3044BC.FWA |
| 3044 | BD | 26.52 | P | P | 1 | B:\BATCH11\3044BD.FWA |
| 3044 | BE | 30.00 | P | P | 1 | B:\BATCH12\3044BE.FWA |
| 3056 | AB | 4.84 | P | P | 1 | B:\BATCH14\3056AB.FWA |
| 3056 | AB | 5.52 | P | P | 1 | B:\BATCH14\3056AB2.FWA |
| 3056 | AC | 1.41 | N | N | 1 | B:\BATCH16\3056AC.FWA |
| 3056 | BC | 1.15 | N | N | 1 | B:\BATCH16\3056BC.FWA |
| 3056 | BC | 1.40 | N | N | 1 | B:\BATCH16\3056BC2.FWA |
| 3056 | BC | 1.13 | N | N | 1 | B:\BATCH16\3056BC3.FWA |
| 3056 | BC | 1.23 | N | N | 1 | B:\BATCH16\3056BC4.FWA |
| 3056 | DE | 2.48 | N | N | 1 | a:\batch40\3056DE1.FWA |
| 3056 | DE | 1.20 | N | N | 1 | a:\batch40\3056DE2.FWA |
| 3057 | AB | 1.55 | N | N | 1 | B:\BATCH15\3057AB.FWA |
| 3057 | AB | 1.71 | N | N | 1 | B:\BATCH15\3057AB2.FWA |
| 3057 | AB | 2.02 | N | N | 1 | B:\BATCH15\3057AB3.FWA |
| 3057 | CD | 1.71 | N | N | 1 | B:\BATCH30\3057CD1.FWA |
| 3057 | CD | 1.10 | N | N | 1 | B:\BATCH30\3057CD2.FWA |
| 3057 | CD | 3.73 | P | P | 1 | B:\BATCH30\3057CD3.FWA |
| 3057 | CD | 1.96 | N | N | 1 | B:\BATCH30\3057CD4.FWA |
| 3057 | DE | 1.68 | N | N | 1 | B:\BATCH35\3057DE1.FWA |
| 3057 | DE | 1.26 | N | N | 1 | B:\BATCH35\3057DE2.FWA |
| 3057 | DE | 1.60 | N | N | 1 | B:\BATCH35\3057DE3.FWA |
| 3061 | BC | 3.76 | N | P | 0 | B:\BATCH30\3061BC1.FWA |
| 3061 | BC | 2.92 | N | N | 1 | B:\BATCH30\3061BC2.FWA |
| 3064 | AB | 1.79 | N | N | 1 | B:\BATCH16\3064AB.FWA |
| 3064 | AB | 3.21 | P | P | 1 | B:\BATCH16\3064AB2.FWA |
| 3064 | CD | 1.80 | N | N | 1 | B:\BATCH37\3064CD1.FWA |
| 3065 | A1 | 5.53 | P | P | 1 | B:\BATCH15\3065A1.FWA |
| 3065 | A2 | 9.51 | P | P | 1 | B:\BATCH15\3065A2.FWA |
| 3065 | A3 | 9.81 | P | P | 1 | B:\BATCH15\3065A3.FWA |





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|---|---|---|---|---|---|---|
| 3065 | A4 | 13.42 | P | P | 1 | B:\BATCH15\3065A4.FWA |
| 3065 | A5 | 12.77 | P | P | 1 | B:\BATCH15\3065A5.FWA |
| 3065 | A6 | 19.32 | P | P | 1 | B:\BATCH15\3065A6.FWA |
| 3065 | A7 | 18.61 | P | P | 1 | B:\BATCH15\3065A7.FWA |
| 3066 | A1 | 2.91 | N | N | 1 | B:\BATCH15\3066A1.FWA |
| 3066 | A2 | 2.34 | N | N | 1 | B:\BATCH15\3066A2.FWA |
| 3066 | A3 | 2.69 | N | N | 1 | B:\BATCH15\3066A3.FWA |
| 3066 | A4 | 2.91 | N | N | 1 | B:\BATCH15\3066A4.FWA |
| 3066 | A5 | 1.73 | N | N | 1 | B:\BATCH15\3066A5.FWA |
| 3072 | BC | 8.85 | P | P | 1 | B:\BATCH30\3072BC1.FWA |
| 3072 | BC | 7.08 | P | P | 1 | B:\BATCH30\3072BC2.FWA |
| 3072 | BC | 3.89 | P | P | 1 | B:\BATCH30\3072BC3.FWA |
| 3072 | BC | 2.14 | N | N | 1 | B:\BATCH30\3072BC4.FWA |
| 3072 | CD | 1.73 | N | N | 1 | A:\BATCH41\3072CD1.FWA |
| 3072 | CD | 2.55 | N | N | 1 | A:\BATCH41\3072CD2.FWA |
| 3072 | CD | 1.89 | N | N | 1 | A:\BATCH41\3072CD3.FWA |
| 3072 | CD | 1.22 | N | N | 1 | A:\BATCH41\3072CD4.FWA |
| 3072 | CD | 1.67 | N | N | 1 | A:\BATCH41\3072CD5.FWA |
| 3072 | CD | 1.81 | N | N | 1 | A:\BATCH41\3072CD6.FWA |
| 3073 | BC | 2.07 | N | N | 1 | B:\BATCH37\3073BC1.FWA |
| 3073 | BC | 2.27 | N | N | 1 | B:\BATCH37\3073BC2.FWA |
| 3073 | BC | 7.24 | P | P | 1 | B:\BATCH37\3073BC3.FWA |
| 3073 | BC | 3.39 | I | P | 0 | B:\BATCH37\3073BC4.FWA |
| 3073 | BC | 4.62 | P | P | 1 | B:\BATCH37\3073BC5.FWA |
| 3105 | AB | 1.04 | N | N | 1 | A:\BATCH41\3105AB1.FWA |
| 3105 | AB | 1.50 | N | N | 1 | A:\BATCH41\3105AB2.FWA |
| 3105 | AB | 1.64 | N | N | 1 | A:\BATCH41\3105AB3.FWA |
| 3105 | AB | 1.80 | N | N | 1 | A:\BATCH41\3105AB4.FWA |
| 3105 | AB | 1.40 | N | N | 1 | A:\BATCH41\3105AB5.FWA |
| 3105 | AB | 1.87 | N | N | 1 | A:\BATCH41\3105AB6.FWA |
| 3106 | AC | 1.52 | N | N | 1 | A:\BATCH41\3106AC1.FWA |
| 3106 | AC | 1.89 | N | N | 1 | A:\BATCH41\3106AC2.FWA |
| 3106 | AC | 1.94 | N | N | 1 | A:\BATCH41\3106AC3.FWA |
| 3106 | AC | 1.44 | N | N | 1 | A:\BATCH41\3106AC4.FWA |
| 3106 | AC | 2.04 | N | N | 1 | A:\BATCH41\3106AC5.FWA |
| 3106 | AC | 1.88 | N | N | 1 | A:\BATCH41\3106AC6.FWA |
| 4040 | AB | 3.09 | I | N | 0 | B:\BATCH8\4040AB.FWA |
| 4040 | AB | 2.97 | N | N | 1 | B:\BATCH8\4040AB1.FWA |
| 4040 | DE | 5.53 | P | P | 1 | B:\BATCH25\4040DE1.FWA |
| 4040 | DE | 7.40 | P | P | 1 | B:\BATCH25\4040DE2.FWA |
| 4040 | DE | 4.28 | P | P | 1 | B:\BATCH25\4040DE3.FWA |
| 4040 | DE | 3.64 | P | P | 1 | B:\BATCH25\4040DE4.FWA |
| 4040 | FG | 1.98 | N | N | 1 | a:\batch39\4040FG1.FWA |
| 4040 | FG | 1.21 | N | N | 1 | a:\batch39\4040FG2.FWA |
| 4040 | FG | 1.20 | N | N | 1 | a:\batch39\4040FG3.FWA |
| 4040 | FG | 3.44 | N | P | 0 | a:\batch39\4040FG4.FWA |
| 4040 | FG | 2.11 | N | N | 1 | a:\batch40\4040FG5.FWA |
| 4040 | FG | 1.33 | N | N | 1 | a:\batch40\4040FG6.FWA |
| 4040 | FG | 1.04 | N | N | 1 | a:\batch40\4040FG7.FWA |
| 4040 | FG | 1.41 | N | N | 1 | a:\batch40\4040FG8.FWA |
| 4040 | FG | 5.12 | P | P | 1 | a:\batch40\4040FG9.FWA |

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|---|---|---|---|---|---|---|
| 4040 | FG | 5.25 | P | P | 1 | a:\batch40\4040FG10.FWA |
| 4040 | FG | 1.98 | N | N | 1 | a:\batch40\4040FG11.FWA |
| 4040 | FG | 1.56 | N | N | 1 | a:\batch40\4040FG12.FWA |
| 4041 | AB | 5.49 | P | P | 1 | B:\BATCH14\4041AB.FWA |
| 4041 | AB | 4.98 | P | P | 1 | B:\BATCH14\4041AB2.FWA |
| 4041 | AB | 4.16 | P | P | 1 | B:\BATCH14\4041AB3.FWA |
| 4041 | AB | 4.49 | P | P | 1 | B:\BATCH14\4041AB4.FWA |
| 4041 | AB | 4.70 | P | P | 1 | B:\BATCH14\4041AB6.FWA |
| 4041 | AB | 4.53 | P | P | 1 | B:\BATCH14\4041AB7.FWA |
| 4041 | BC | 4.66 | P | P | 1 | B:\BATCH17\4041BC.FWA |
| 4041 | BC | 2.01 | N | N | 1 | B:\BATCH17\4041BC2.FWA |
| 4041 | BC | 2.03 | N | N | 1 | B:\BATCH17\4041BC3.FWA |
| 4041 | BC | 4.89 | P | P | 1 | B:\BATCH17\4041BC4.FWA |
| 4041 | BC | 6.08 | P | P | 1 | B:\BATCH17\4041BC5.FWA |
| 4041 | BC | 3.83 | P | P | 1 | B:\BATCH17\4041BC6.FWA |
| 4041 | BC | 5.22 | P | P | 1 | B:\BATCH17\4041BC7.FWA |
| 4041 | BC | 2.18 | N | N | 1 | B:\BATCH17\4041BC8.FWA |
| 4045 | AB | 1.35 | N | N | 1 | B:\BATCH14\4045AB5.FWA |
| 4045 | AB | 5.55 | P | P | 1 | B:\BATCH7\4045AB.FWA |
| 4045 | CD | 4.48 | P | P | 1 | B:\BATCH25\4045CD1.FWA |
| 4045 | CD | 3.50 | P | P | 1 | B:\BATCH25\4045CD2.FWA |
| 4045 | CD | 3.30 | P | P | 1 | B:\BATCH25\4045CD3.FWA |
| 4045 | CD | 4.34 | P | P | 1 | B:\BATCH25\4045CD4.FWA |
| 4045 | CD | 5.49 | P | P | 1 | B:\BATCH25\4045CD5.FWA |
| 4045 | DE | 5.43 | P | P | 1 | a:\batch40\4045DE1.FWA |
| 4045 | DE | 4.20 | P | P | 1 | a:\batch40\4045DE2.FWA |
| 4045 | DE | 2.47 | N | N | 1 | a:\batch40\4045DE3.FWA |
| 4045 | DE | 2.42 | N | N | 1 | a:\batch40\4045DE4.FWA |
| 4045 | DE | 4.78 | P | P | 1 | a:\batch40\4045DE5.FWA |
| 4045 | DE | 2.28 | N | N | 1 | a:\batch40\4045DE6.FWA |
| 4059 | AB | 0.76 | N | N | 1 | B:\BATCH17\4059AB.FWA |
| 4059 | AB | 1.02 | N | N | 1 | B:\BATCH17\4059AB2.FWA |
| 4059 | AB | 1.82 | N | N | 1 | B:\BATCH17\4059AB3.FWA |
| 5062 | AB | 5.73 | P | P | 1 | B:\BATCH16\5062AB.FWA |
| 5062 | AB | 4.39 | P | P | 1 | B:\BATCH16\5062AB2.FWA |
| 5062 | AB | 4.81 | P | P | 1 | B:\BATCH16\5062AB3.FWA |
| 5062 | AB | 1.91 | N | N | 1 | B:\BATCH16\5062AB4.FWA |
| 5063 | AB | 1.12 | N | N | 1 | B:\BATCH16\5063AB.FWA |
| 5063 | AB | 0.94 | N | N | 1 | B:\BATCH16\5063AB2.FWA |
| 7074 | BC | 2.00 | N | N | 1 | B:\BATCH30\7074BCA1.FWA |
| 7074 | BC | 4.49 | P | P | 1 | B:\BATCH30\7074BCA2.FWA |
| 7074 | BC | 4.81 | P | P | 1 | B:\BATCH30\7074BCA3.FWA |
| 7074 | BC | 2.97 | I | N | 0 | B:\BATCH30\7074BCA4.FWA |
| 7074 | BC | 1.86 | N | N | 1 | B:\BATCH30\7074BCA5.FWA |
| 7074 | BC | 3.38 | I | P | 0 | B:\BATCH30\7074BCA6.FWA |
| 7074 | BC | 1.68 | N | N | 1 | B:\BATCH30\7074BCA7.FWA |
| 7074 | BC | 1.91 | N | N | 1 | B:\BATCH30\7074BCA8.FWA |
| 7074 | CD | 4.37 | P | P | 1 | B:\BATCH36\7074CD1.FWA |
| 7074 | CD | 3.72 | P | P | 1 | B:\BATCH36\7074CD2.FWA |
| 7074 | CD | 7.71 | P | P | 1 | B:\BATCH36\7074CD3.FWA |
| 7074 | CD | 6.95 | P | P | 1 | B:\BATCH36\7074CD4.FWA |





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|---|---|---|---|---|---|---|
| 7074 | DF | 1.41 | N | N | 1 | A:\BATCH41\7074DF1.FWA |
| 7074 | DF | 2.88 | N | N | 1 | A:\BATCH41\7074DF2.FWA |
| 7074 | DF | 2.54 | N | N | 1 | A:\BATCH41\7074DF3.FWA |
| 7074 | DF | 2.13 | N | N | 1 | A:\BATCH41\7074DF4.FWA |
| 7074 | DF | -0.76 | N | N | 1 | A:\BATCH41\7074DF5.FWA |
| 7074 | DF | 0.49 | N | N | 1 | A:\BATCH41\7074DF6.FWA |
| 7075 | AC | 1.84 | N | N | 1 | B:\BATCH35\7075AC1.FWA |
| 7075 | AC | 5.25 | P | P | 1 | B:\BATCH35\7075AC2.FWA |
| 7075 | AC | 2.56 | N | N | 1 | B:\BATCH35\7075AC3.FWA |
| 7075 | AC | 2.93 | I | N | 0 | B:\BATCH35\7075AC4.FWA |
| 7075 | CE | 1.75 | N | N | 1 | A:\BATCH41\7075CE1.FWA |
| 7075 | CE | 2.94 | N | N | 1 | A:\BATCH41\7075CE2.FWA |
| 7075 | CE | 1.88 | N | N | 1 | A:\BATCH41\7075CE3.FWA |
| 7075 | CE | 1.73 | N | N | 1 | A:\BATCH41\7075CE4.FWA |
| 7075 | CE | 4.82 | P | P | 1 | A:\BATCH41\7075CE5.FWA |
| 7075 | CE | 1.73 | N | N | 1 | A:\BATCH41\7075CE6.FWA |
| 7076 | AC | 5.62 | P | P | 1 | B:\BATCH33\7076AC1.FWA |
| 7076 | AC | 4.90 | P | P | 1 | B:\BATCH33\7076AC2.FWA |
| 7076 | AC | 4.16 | P | P | 1 | B:\BATCH33\7076AC3.FWA |
| 7076 | CD | 5.02 | P | P | 1 | B:\BATCH36\7076CD1.FWA |
| 7076 | CD | 3.54 | P | P | 1 | B:\BATCH36\7076CD2.FWA |
| 7076 | CD | 4.59 | P | P | 1 | B:\BATCH36\7076CD3.FWA |
| 7076 | CD | 5.70 | P | P | 1 | B:\BATCH36\7076CD4.FWA |
| 7077 | AC | 3.63 | N | P | 0 | B:\BATCH33\7077AC1.FWA |
| 7077 | AC | 2.98 | N | N | 1 | B:\BATCH33\7077AC2.FWA |
| 7077 | AC | 5.10 | P | P | 1 | B:\BATCH33\7077AC3.FWA |
| 7077 | AC | 3.38 | N | P | 0 | B:\BATCH33\7077AC4.FWA |
| 7078 | AC | 3.36 | I | P | 0 | B:\BATCH33\7078AC1.FWA |
| 7078 | AC | 2.80 | N | N | 1 | B:\BATCH33\7078AC2.FWA |
| 7078 | AC | 2.23 | N | N | 1 | B:\BATCH33\7078AC3.FWA |
| 7078 | AC | 2.00 | N | N | 1 | B:\BATCH33\7078AC4.FWA |
| 7078 | CE | 1.43 | N | N | 1 | A:\BATCH42\7078CE1.FWA |
| 7078 | CE | 1.70 | N | N | 1 | A:\BATCH42\7078CE2.FWA |
| 7092 | AC | 4.25 | P | P | 1 | B:\BATCH36\7092AC1.FWA |
| 7092 | AC | 2.81 | N | N | 1 | B:\BATCH36\7092AC2.FWA |
| 7092 | AC | 4.96 | P | P | 1 | B:\BATCH36\7092AC3.FWA |
| 7092 | AC | 2.95 | N | N | 1 | B:\BATCH36\7092AC4.FWA |
| 7092 | CD | 1.70 | N | N | 1 | A:\BATCH41\7092CD.FWA |
| 7092 | CD | 1.65 | N | N | 1 | A:\BATCH41\7092CD3.FWA |
| 7093 | AC | 5.72 | P | P | 1 | B:\BATCH33\7093AC1.FWA |
| 7093 | AC | 4.04 | P | P | 1 | B:\BATCH33\7093AC2.FWA |
| 7093 | AC | 1.67 | N | N | 1 | B:\BATCH33\7093AC3.FWA |
| 7093 | CE | 2.88 | N | N | 1 | B:\BATCH38\7093CE1.FWA |
| 7093 | CE | 2.05 | N | N | 1 | B:\BATCH38\7093CE2.FWA |
| 7093 | CE | 1.72 | N | N | 1 | B:\BATCH38\7093CE3.FWA |
| 7093 | CE | 2.13 | N | N | 1 | B:\BATCH38\7093CE4.FWA |
| 7094 | AC | 1.58 | N | N | 1 | A:\BATCH41\7094AC1.FWA |
| 7094 | AC | 2.67 | N | N | 1 | A:\BATCH41\7094AC2.FWA |
| 7094 | AC | 2.50 | N | N | 1 | A:\BATCH41\7094AC3.FWA |
| 7094 | AC | 2.12 | N | N | 1 | A:\BATCH41\7094AC4.FWA |
| 7094 | AC | 1.74 | N | N | 1 | A:\BATCH41\7094AC5.FWA |

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|---|---|---|---|---|---|---|
| 7094 | AC | 4.87 | P | P | 1 | A:\BATCH41\7094AC6.FWA |
| 7095 | AD | 1.60 | N | N | 1 | A:\BATCH42\7095AD1.FWA |
| 7095 | AD | 5.39 | P | P | 1 | A:\BATCH42\7095AD2.FWA |
| 7095 | AD | 1.81 | N | N | 1 | A:\BATCH42\7095AD3.FWA |
| 7095 | AD | 1.47 | N | N | 1 | A:\BATCH42\7095AD4.FWA |
| 7095 | AD | 1.31 | N | N | 1 | A:\BATCH42\7095AD5.FWA |
| 7095 | AD | 1.63 | N | N | 1 | A:\BATCH42\7095AD6.FWA |
| 7095 | C1 | 1.02 | N | N | 1 | a:\batch39\7095C1A.FWA |
| 7095 | C1 | 1.58 | N | N | 1 | a:\batch39\7095C1B.FWA |
| 7096 | AC | 1.96 | N | N | 1 | A:\BATCH41\7096AC1.FWA |
| 7096 | AC | 1.61 | N | N | 1 | A:\BATCH41\7096AC2.FWA |
| 7096 | AC | 1.73 | N | N | 1 | A:\BATCH41\7096AC3.FWA |
| 7096 | AC | 1.84 | N | N | 1 | A:\BATCH41\7096AC4.FWA |
| 7096 | AC | 1.28 | N | N | 1 | A:\BATCH41\7096AC5.FWA |
| 7096 | AC | 2.57 | N | N | 1 | A:\BATCH41\7096AC6.FWA |
| 7096 | B1 | 1.38 | N | N | 1 | a:\batch39\7096B1A.FWA |
| 7096 | B1 | 1.18 | N | N | 1 | a:\batch39\7096B1B.FWA |
| 7097 | AC | 1.89 | N | N | 1 | A:\BATCH41\7097AC1.FWA |
| 7097 | AC | 4.13 | N | P | 0 | A:\BATCH41\7097AC2.FWA |
| 7097 | AC | 2.53 | N | N | 1 | A:\BATCH41\7097AC3.FWA |
| 7097 | AC | 2.31 | N | N | 1 | A:\BATCH41\7097AC4.FWA |
| 7097 | AC | 2.53 | N | N | 1 | A:\BATCH41\7097AC5.FWA |
| 7097 | AC | 2.68 | N | N | 1 | A:\BATCH41\7097AC6.FWA |
| 7097 | B1 | 2.18 | N | N | 1 | a:\batch39\7097B1A.FWA |
| 7097 | B1 | 7.25 | P | P | 1 | a:\batch39\7097B1B.FWA |
| 8053 | BC | 2.31 | N | N | 1 | B:\BATCH24\8053BC1.FWA |
| 8053 | BC | 1.75 | N | N | 1 | B:\BATCH24\8053BC2.FWA |
| 8053 | BC | 2.76 | N | N | 1 | B:\BATCH24\8053BC3.FWA |
| 8053 | BC | 2.12 | N | N | 1 | B:\BATCH24\8053BC4.FWA |
| 8053 | CD | 3.53 | N | P | 0 | B:\BATCH31\8053CD1.FWA |
| 8053 | CD | 2.37 | N | N | 1 | B:\BATCH31\8053CD2.FWA |
| 8053 | CD | 2.48 | N | N | 1 | B:\BATCH31\8053CD3.FWA |
| 8053 | CD | 2.06 | N | N | 1 | B:\BATCH31\8053CD4.FWA |
| 8053 | CD | 1.76 | N | N | 1 | B:\BATCH31\8053CD5.FWA |
| 8053 | DE | 2.28 | N | N | 1 | B:\BATCH34\8053DE1.FWA |
| 8053 | DE | 2.24 | N | N | 1 | B:\BATCH34\8053DE2.FWA |
| 8053 | DE | 1.19 | N | N | 1 | B:\BATCH34\8053DE3.FWA |
| 8053 | EF | 1.96 | N | N | 1 | a:\batch40\8053EF1.FWA |
| 8053 | EF | 2.03 | N | N | 1 | a:\batch40\8053EF2.FWA |
| 8053 | EF | 2.07 | N | N | 1 | a:\batch40\8053EF3.FWA |
| 8053 | EF | 1.99 | N | N | 1 | a:\batch40\8053EF4.FWA |
| 8053 | EF | 1.80 | N | N | 1 | a:\batch40\8053EF5.FWA |
| 8053 | EF | 1.53 | N | N | 1 | a:\batch40\8053EF6.FWA |
| 8054 | BC | 2.09 | N | N | 1 | B:\BATCH24\8054BC1.FWA |
| 8054 | BC | 1.80 | N | N | 1 | B:\BATCH24\8054BC2.FWA |
| 8054 | BC | 4.10 | P | P | 1 | B:\BATCH24\8054BC3.FWA |
| 8054 | BC | 3.38 | I | P | 0 | B:\BATCH24\8054BC4.FWA |
| 8054 | BC | 5.52 | P | P | 1 | B:\BATCH24\8054BC5.FWA |
| 8054 | BC | 3.17 | N | N | 1 | B:\BATCH24\8054BC6.FWA |
| 8054 | BC | 3.18 | N | N | 1 | B:\BATCH24\8054BC7.FWA |
| 8054 | BC | 3.94 | P | P | 1 | B:\BATCH24\8054BC8.FWA |





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|---|---|---|---|---|---|---|
| 8054 | CD | 1.66 | N | N | 1 | B:\BATCH31\8054CD1.FWA |
| 8054 | CD | 1.53 | N | N | 1 | B:\BATCH31\8054CD2.FWA |
| 8054 | DE | 3.69 | P | P | 1 | B:\BATCH34\8054DE.FWA |
| 8054 | DE | 2.90 | N | N | 1 | B:\BATCH34\8054DE2.FWA |
| 8054 | DE | 2.00 | N | N | 1 | B:\BATCH34\8054DE3.FWA |
| 8054 | DE | 2.13 | N | N | 1 | B:\BATCH34\8054DE4.FWA |
| 8054 | EF | 2.02 | N | N | 1 | a:\batch40\8054EF1.FWA |
| 8054 | EF | 1.60 | N | N | 1 | a:\batch40\8054EF2.FWA |
| 8054 | EF | 2.05 | N | N | 1 | a:\batch40\8054EF3.FWA |
| 8054 | EF | 2.10 | N | N | 1 | a:\batch40\8054EF4.FWA |
| 8054 | EF | 2.18 | N | N | 1 | a:\batch40\8054EF5.FWA |
| 8054 | EF | 1.67 | N | N | 1 | a:\batch40\8054EF6.FWA |
| 9098 | AC | 2.62 | N | N | 1 | A:\BATCH42\9098AC1.FWA |
| 9098 | AC | 5.69 | I | P | 0 | A:\BATCH42\9098AC2.FWA |
| 9098 | AC | 1.00 | N | N | 1 | A:\BATCH42\9098AC3.FWA |
| 9098 | AC | 1.82 | N | N | 1 | A:\BATCH42\9098AC4.FWA |
| 9098 | AC | 1.35 | N | N | 1 | A:\BATCH42\9098AC5.FWA |
| 9098 | AC | 4.98 | I | P | 0 | A:\BATCH42\9098AC6.FWA |
| 9999 | | 35.36 | P | P | 1 | B:\BATCH10\MILKSOCK.FWA |
| 9999 | | 2.53 | N | N | 1 | B:\BATCH11\BLNK0729.FWA |
| 9999 | | 1.43 | N | N | 1 | B:\BATCH13\TB0815.FWA |
| 9999 | | 1.45 | N | N | 1 | B:\BATCH13\TB08152.FWA |
| 9999 | | 4.14 | N | P | 0 | B:\BATCH14\JJBLNK.FWA |
| 9999 | | 2.20 | N | N | 1 | B:\BATCH14\TB0824.FWA |
| 9999 | | 1.81 | I | N | 0 | B:\BATCH14\TB08242.FWA |
| 9999 | | 1.83 | N | N | 1 | B:\BATCH15\JS0831.FWA |
| 9999 | | 2.81 | N | N | 1 | B:\BATCH21\TB1221.FWA |
| 9999 | | 2.95 | N | N | 1 | B:\BATCH21\TB1221B.FWA |
| 9999 | | 3.13 | N | N | 1 | B:\BATCH21\TB1221C.FWA |
| 9999 | | 7.76 | P | P | 1 | B:\BATCH21\TB1221D.FWA |
| 9999 | | 8.62 | P | P | 1 | B:\BATCH21\TB1221E.FWA |
| 9999 | | 7.83 | P | P | 1 | B:\BATCH21\TB1221F.FWA |
| 9999 | | 5.28 | P | P | 1 | B:\BATCH21\TB1221G.FWA |
| 9999 | | 3.18 | N | N | 1 | B:\BATCH21\TB1221H.FWA |
| 9999 | | 2.53 | N | N | 1 | B:\BATCH21\TB1221I.FWA |
| 9999 | | 3.16 | N | N | 1 | B:\BATCH21\TB1221J.FWA |
| 9999 | | 5.18 | P | P | 1 | B:\BATCH24\TB0112A.FWA |
| 9999 | | 2.26 | N | N | 1 | B:\BATCH24\TB0112B.FWA |
| 9999 | | 1.84 | N | N | 1 | B:\BATCH24\TB0112C.FWA |
| 9999 | | 2.06 | N | N | 1 | B:\BATCH24\TB0112D.FWA |
| 9999 | | 1.54 | N | N | 1 | B:\BATCH25\TB0125A.FWA |
| 9999 | | 1.58 | N | N | 1 | B:\BATCH25\TB0125B.FWA |
| 9999 | | 1.82 | N | N | 1 | B:\BATCH25\TB0125C.FWA |
| 9999 | | 2.05 | N | N | 1 | B:\BATCH25\TB0125D.FWA |
| 9999 | | 2.25 | N | N | 1 | B:\BATCH25\TB0125E.FWA |
| 9999 | | 1.69 | N | N | 1 | B:\BATCH25\TB0125F.FWA |
| 9999 | | 2.21 | N | N | 1 | B:\BATCH25\TB0125HA.FWA |
| 9999 | | 2.78 | N | N | 1 | B:\BATCH25\TB0125HB.FWA |
| 9999 | | 2.12 | N | N | 1 | B:\BATCH25\TB0125HC.FWA |
| 9999 | | 2.36 | N | N | 1 | B:\BATCH25\TB0125HD.FWA |
| 9999 | | 2.50 | N | N | 1 | B:\BATCH25\TB0125HE.FWA |

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|---|---|---|---|---|---|
| 9999 | 1.98 | N | N | 1 | B:\BATCH25\TB0125HF.FWA |
| 9999 | 2.10 | N | N | 1 | B:\BATCH26\TB0201A.FWA |
| 9999 | 1.35 | N | N | 1 | B:\BATCH26\TB0201B.FWA |
| 9999 | 2.14 | N | N | 1 | B:\BATCH26\TB0201C.FWA |
| 9999 | 2.19 | N | N | 1 | B:\BATCH26\TB0201E.FWA |
| 9999 | 2.26 | N | N | 1 | B:\BATCH26\TB0201F.FWA |
| 9999 | 2.33 | N | N | 1 | B:\BATCH26\TB0201G.FWA |
| 9999 | 2.26 | N | N | 1 | B:\BATCH26\TB0201H.FWA |
| 9999 | 2.29 | N | N | 1 | B:\BATCH26\TB02021D.FWA |
| 9999 | 1.77 | N | N | 1 | B:\BATCH3\BLNK0414.FWA |
| 9999 | 2.16 | N | N | 1 | B:\BATCH35\LOTIBLN2.FWA |
| 9999 | 2.32 | N | N | 1 | B:\BATCH35\LOTIBLNK.FWA |
| 9999 | 3.14 | N | N | 1 | B:\BATCH4\TTDC0426.FWA |
| 9999 | 7.15 | P | P | 1 | B:\BATCH6\SPONG.FWA |
| 9999 | 4.25 | P | P | 1 | B:\BATCH7\ALEY1.FWA |
| 9999 | 2.92 | N | N | 1 | B:\BATCH8\JOHNBLNK.FWA |
| 9999 | 2.42 | N | N | 1 | B:\BATCH8\MPCACOTT.FWA |





| Location Number | Event | OBI | Exposure (days) | Number of scans |
|---|---|---|---|---|
| 0 | BB | 3.10 | 0 | 1 |
| 1002 | BD | 4.50 | 36 | 1 |
| 1002 | CD | 0.95 | 2 | 3 |
| 1002 | EF | 3.17 | 59 | 5 |
| 1002 | FG | 2.41 | 136 | 6 |
| 1002 | GH | 3.05 | 60 | 5 |
| 1002 | HI | 7.81 | 64 | 3 |
| 1002 | IJ | 1.91 | 69 | 2 |
| 1003 | BD | 0.88 | 77 | 2 |
| 1003 | CD | 1.48 | 2 | 3 |
| 1003 | DE | 1.72 | 59 | 5 |
| 1003 | FG | 1.76 | 54 | 5 |
| 1003 | GH | 3.67 | 30 | 6 |
| 1003 | HI | 3.13 | 49 | 4 |
| 1003 | IJ | 2.02 | 53 | 2 |
| 1005 | CD | 2.61 | 147 | 2 |
| 1006 | AC | 2.68 | 34 | 2 |
| 1006 | BC | 3.47 | 20 | 2 |
| 1006 | BD | 1.32 | 40 | 2 |
| 1006 | EF | 1.67 | 72 | 4 |
| 1006 | FG | 3.59 | 99 | 3 |
| 1006 | GH | 2.15 | 116 | 1 |
| 1006 | HI | 3.58 | 44 | 2 |
| 1007 | BC | 0.94 | 33 | 1 |
| 1007 | CD | 2.47 | 97 | 1 |
| 1007 | DE | 2.06 | 72 | 2 |
| 1007 | FG | 2.22 | 116 | 4 |
| 1008 | BC | 2.06 | 58 | 1 |
| 1009 | BC | 22.89 | 141 | 2 |
| 1013 | BC | 1.33 | 57 | 3 |
| 1014 | BC | 3.50 | 42 | 1 |
| 1016 | AC | 0.98 | 58 | 1 |
| 1021 | AB | 3.67 | 50 | 1 |
| 1021 | CD | 8.89 | 57 | 3 |
| 1021 | EF | 11.20 | 135 | 8 |
| 1021 | FG | 2.59 | 172 | 4 |
| 1024 | AB | 4.69 | 20 | 2 |
| 1026 | AB | 2.44 | 77 | 1 |
| 1026 | CD | 2.19 | 147 | 5 |
| 1026 | DE | 3.97 | 160 | 4 |
| 1028 | AC | 2.10 | 35 | 1 |
| 1028 | BC | 2.77 | 2 | 4 |
| 1028 | DE | 1.53 | 101 | 1 |
| 1028 | EF | 4.53 | 136 | 4 |
| 1028 | FG | 3.85 | 60 | 2 |
| 1028 | GH | 3.20 | 30 | 3 |
| 1029 | AB | 1.72 | 136 | 3 |
| 1029 | BC | 4.57 | 71 | 5 |
| 1029 | CE | 2.00 | 121 | 4 |

| | | | | |
|---|---|---|---|---|
| 1030 | AC | 1.20 | 122 | 7 |
| 1030 | DE | 1.76 | 113 | 4 |
| 1030 | EF | 2.53 | 86 | 4 |
| 1030 | FG | 1.95 | 90 | 4 |
| 1031 | AC | 2.26 | 17 | 3 |
| 1031 | AE | 2.71 | 39 | 3 |
| 1031 | CE | 3.14 | 22 | 2 |
| 1031 | EF | 1.75 | 2 | 2 |
| 1031 | GH | 3.12 | 93 | 4 |
| 1031 | HI | 1.73 | 62 | 3 |
| 1033 | AB | 1.18 | 46 | 1 |
| 1033 | CD | 1.51 | 64 | 4 |
| 1033 | DE | 1.60 | 135 | 5 |
| 1034 | BD | 1.51 | 2 | 2 |
| 1034 | EF | 2.71 | 71 | 7 |
| 1034 | FG | 2.54 | 126 | 6 |
| 1034 | GH | 4.87 | 55 | 4 |
| 1035 | AB | 2.02 | 2 | 2 |
| 1035 | CD | 3.71 | 90 | 5 |
| 1035 | DE | 2.48 | 155 | 7 |
| 1035 | EF | 3.07 | 71 | 4 |
| 1036 | AB | 2.26 | 2 | 1 |
| 1036 | CD | 5.30 | 112 | 4 |
| 1036 | DE | 3.79 | 64 | 6 |
| 1037 | AD | 2.63 | 90 | 3 |
| 1037 | BC | 1.76 | 2 | 3 |
| 1037 | DE | 3.69 | 106 | 3 |
| 1037 | EF | 3.67 | 100 | 4 |
| 1037 | FG | 4.69 | 96 | 4 |
| 1038 | AB | 2.16 | 2 | 1 |
| 1038 | CD | 2.98 | 114 | 4 |
| 1038 | DE | 2.21 | 82 | 4 |
| 1038 | EF | 3.03 | 65 | 3 |
| 1039 | AB | 8.53 | 2 | 1 |
| 1039 | AC | 3.70 | 77 | 4 |
| 1039 | CD | 2.56 | 23 | 4 |
| 1039 | DE | 6.25 | 112 | 4 |
| 1039 | EF | 4.69 | 64 | 5 |
| 1039 | FG | 4.74 | 96 | 5 |
| 1046 | BC | 8.43 | 181 | 5 |
| 1046 | CD | 14.41 | 181 | 1 |
| 1047 | AB | 0.96 | 3 | 2 |
| 1047 | AC | 3.88 | 63 | 4 |
| 1047 | CD | 2.83 | 147 | 6 |
| 1047 | DE | 2.67 | 147 | 4 |
| 1048 | AB | 1.22 | 3 | 2 |
| 1048 | AC | 2.84 | 57 | 4 |
| 1048 | CD | 4.95 | 112 | 5 |
| 1048 | DE | 1.40 | 207 | 6 |
| 1049 | AB | -0.70 | 3 | 1 |
| 1049 | AC | 1.58 | 57 | 2 |





| | | | | |
|---|---|---|---|---|
| 1049 | CD | 3.06 | 104 | 6 |
| 1049 | DE | 2.10 | 215 | 6 |
| 1050 | AB | 1.32 | 2 | 2 |
| 1050 | AC | 1.40 | 56 | 4 |
| 1050 | CD | 2.26 | 68 | 6 |
| 1051 | AB | 2.78 | 61 | 3 |
| 1051 | BC | 2.18 | 127 | 2 |
| 1051 | CD | 3.55 | 180 | 4 |
| 1052 | AB | 3.41 | 51 | 2 |
| 1052 | BC | 3.98 | 133 | 4 |
| 1058 | AB | 1.71 | 140 | 3 |
| 1058 | C | 2.20 | 140 | 1 |
| 1060 | AB | 2.11 | 135 | 4 |
| 1069 | AB | 3.00 | 51 | 5 |
| 1069 | BD | 4.14 | 146 | 4 |
| 1069 | CD | 2.02 | 107 | 4 |
| 1079 | BC | 4.02 | 112 | 5 |
| 1079 | CD | 2.00 | 42 | 2 |
| 1080 | AB | 3.35 | 50 | 6 |
| 1080 | CD | 3.07 | 93 | 4 |
| 1081 | AB | 4.11 | 44 | 8 |
| 1081 | AC | 2.25 | 79 | 4 |
| 1081 | BC | 2.02 | 35 | 2 |
| 1082 | AB | 4.81 | 68 | 4 |
| 1082 | BC | 4.18 | 146 | 6 |
| 1083 | AB | 3.72 | 68 | 4 |
| 1083 | BD | 5.68 | 146 | 6 |
| 1084 | AB | 3.04 | 63 | 5 |
| 1084 | AC | 3.45 | 82 | 3 |
| 1084 | BD | 6.97 | 112 | 1 |
| 1087 | AB | 1.20 | 98 | 5 |
| 1087 | BC | 2.39 | 78 | 2 |
| 1088 | AB | 4.03 | 22 | 6 |
| 1088 | BC | 2.44 | 132 | 6 |
| 1089 | AB | 4.23 | 85 | 3 |
| 1089 | BC | 3.50 | 69 | 2 |
| 1090 | AD | 3.55 | 112 | 4 |
| 1102 | AB | 3.58 | 78 | 5 |
| 1102 | BC | 5.74 | 54 | 2 |
| 1103 | AB | 3.67 | 78 | 2 |
| 3017 | BC | 3.50 | 64 | 7 |
| 3017 | BD | 4.12 | 75 | 4 |
| 3017 | BE | 3.88 | 102 | 4 |
| 3017 | DF | 2.80 | 152 | 4 |
| 3017 | EF | 3.61 | 125 | 5 |
| 3018 | AB | 1.16 | 25 | 1 |
| 3018 | CD | 1.74 | 151 | 2 |
| 3019 | AB | 1.29 | 25 | 1 |
| 3019 | CD | 1.69 | 151 | 4 |
| 3020 | AB | 8.93 | 25 | 2 |
| 3020 | CD | 23.24 | 26 | 1 |

| | | | | |
|---|---|---|---|---|
| 3043 | CD | 1.79 | 104 | 4 |
| 3044 | BC | 34.87 | 1 | 1 |
| 3044 | BD | 26.52 | 1 | 1 |
| 3044 | BE | 30.00 | 7 | 1 |
| 3056 | AB | 5.18 | 19 | 2 |
| 3056 | AC | 1.41 | 61 | 1 |
| 3056 | BC | 1.23 | 42 | 4 |
| 3056 | DE | 1.84 | 119 | 2 |
| 3057 | AB | 1.76 | 26 | 3 |
| 3057 | CD | 2.13 | 146 | 4 |
| 3057 | DE | 1.51 | 87 | 3 |
| 3061 | BC | 3.34 | 149 | 2 |
| 3064 | AB | 2.50 | 41 | 2 |
| 3064 | CD | 1.80 | 91 | 1 |
| 3065 | A1 | 5.53 | 0 | 1 |
| 3065 | A2 | 9.51 | 0 | 1 |
| 3065 | A3 | 9.81 | 0 | 1 |
| 3065 | A4 | 13.42 | 0 | 1 |
| 3065 | A5 | 12.77 | 0 | 1 |
| 3065 | A6 | 19.32 | 0 | 1 |
| 3065 | A7 | 18.61 | 0 | 1 |
| 3066 | A1 | 2.91 | 0 | 1 |
| 3066 | A2 | 2.34 | 0 | 1 |
| 3066 | A3 | 2.69 | 0 | 1 |
| 3066 | A4 | 2.91 | 0 | 1 |
| 3066 | A5 | 1.73 | 0 | 1 |
| 3072 | BC | 5.49 | 27 | 4 |
| 3072 | CD | 1.81 | 125 | 6 |
| 3073 | BC | 3.92 | 91 | 5 |
| 3105 | AB | 1.54 | 33 | 6 |
| 3106 | AC | 1.79 | 33 | 6 |
| 4040 | AB | 3.03 | 18 | 2 |
| 4040 | DE | 5.21 | 163 | 4 |
| 4040 | FG | 2.30 | 125 | 12 |
| 4041 | AB | 4.73 | 96 | 6 |
| 4041 | BC | 3.86 | 64 | 8 |
| 4045 | AB | 3.45 | 96 | 2 |
| 4045 | CD | 4.22 | 163 | 5 |
| 4045 | DE | 3.60 | 153 | 6 |
| 4059 | AB | 1.20 | 64 | 3 |
| 5062 | AB | 4.21 | 41 | 4 |
| 5063 | AB | 1.03 | 41 | 2 |
| 7074 | BC | 2.89 | 21 | 8 |
| 7074 | CD | 5.69 | 89 | 4 |
| 7074 | DF | 1.45 | 37 | 6 |
| 7075 | AC | 3.15 | 92 | 4 |
| 7075 | CE | 2.48 | 40 | 6 |
| 7076 | AC | 4.89 | 63 | 3 |
| 7076 | CD | 4.71 | 33 | 4 |
| 7077 | AC | 3.77 | 63 | 4 |
| 7078 | AC | 2.60 | 63 | 4 |





| | | | | |
|---|---|---|---|---|
| 7078 | CE | 1.57 | 69 | 2 |
| 7092 | AC | 3.74 | 93 | 4 |
| 7092 | CD | 1.68 | 37 | 2 |
| 7093 | AC | 3.81 | 59 | 3 |
| 7093 | CE | 2.20 | 43 | 4 |
| 7094 | AC | 2.58 | 40 | 6 |
| 7095 | AD | 2.20 | 40 | 6 |
| 7095 | C1 | 1.30 | 0 | 2 |
| 7096 | AC | 1.83 | 27 | 6 |
| 7096 | B1 | 1.28 | 0 | 2 |
| 7097 | AC | 2.68 | 27 | 6 |
| 7097 | B1 | 4.72 | 0 | 2 |
| 8053 | BC | 2.24 | 106 | 4 |
| 8053 | CD | 2.44 | 70 | 5 |
| 8053 | DE | 1.90 | 61 | 3 |
| 8053 | EF | 1.90 | 36 | 6 |
| 8054 | BC | 3.40 | 106 | 8 |
| 8054 | CD | 1.60 | 70 | 2 |
| 8054 | DE | 2.68 | 61 | 4 |
| 8054 | EF | 1.94 | 36 | 6 |
| 9098 | AC | 2.91 | 26 | 6 |

TABLE 3. SELECTED ANALYTICAL DATA SORTED BY COMMUNITY (CC)

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| | cc | site | date | temp | ph | eh | cond | bac | no | nh | cl | so | obi | x | y | z |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 1021 | 95165 | 10.2 | 7.2 | 147 | 978 | 0 | 12 | . | 88 | 34 | 22.0 | . | . | . |
| 2 | 10 | 1026 | 95165 | 10.7 | 7.1 | 152 | 1056 | 0 | 11 | . | 98 | 45 | 6.3 | . | . | . |
| 3 | 10 | 1051 | 95166 | 10.1 | 7.3 | 137 | 1962 | 1 | 13 | . | 344 | 49 | 4.5 | . | . | . |
| 4 | 11 | 1029 | 94010 | . | . | . | . | 0 | 13 | . | . | . | 2.0 | . | . | . |
| 5 | 11 | 1029 | 95002 | 9.4 | 7.1 | 164 | 966 | 0 | 12 | . | 92 | 32 | 7.1 | . | . | . |
| 6 | 11 | 1030 | 94083 | . | . | . | . | 0 | 20 | . | . | . | 1.7 | . | . | . |
| 7 | 11 | 1030 | 95140 | 9.8 | 7.5 | 165 | 777 | 0 | 22 | . | 21 | 35 | 2.4 | . | . | . |
| 8 | 11 | 1031 | 94083 | . | . | . | . | 0 | 20 | . | . | . | 2.8 | . | . | . |
| 9 | 11 | 1031 | 95111 | 9.4 | 7.4 | 151 | 781 | 0 | 22 | . | 32 | 39 | 5.8 | . | . | . |
| 10 | 11 | 1034 | 94119 | . | . | . | . | 1 | 8 | . | . | . | 3.3 | . | . | . |
| 11 | 11 | 1034 | 95104 | 9.4 | 7.7 | 166 | 602 | 1 | 7 | . | 14 | 28 | 5.5 | . | . | . |
| 12 | 11 | 1034 | 95181 | 10.3 | 7.6 | 123 | 426 | 1 | 7 | . | 12 | 27 | 4.0 | . | . | . |
| 13 | 11 | 1037 | 94147 | 11.9 | 6.5 | 124 | 1201 | 0 | 7 | . | . | . | 2.9 | . | . | . |
| 14 | 11 | 1037 | 95152 | 10.9 | 7.3 | 149 | 1165 | 0 | 8 | . | 139 | 31 | 6.2 | . | . | . |
| 15 | 11 | 1069 | 95003 | 10.5 | 7.1 | 138 | 838 | 0 | 10 | . | 67 | 31 | 4.0 | . | . | . |
| 16 | 11 | 1069 | 95153 | 10.9 | 7.5 | 159 | 793 | 0 | 10 | . | 58 | 30 | 5.4 | . | . | . |
| 17 | 11 | 1080 | 95002 | 10.0 | 7.1 | 140 | 838 | 0 | 10 | . | 68 | 28 | 5.5 | . | . | . |
| 18 | 11 | 1080 | 95139 | 10.4 | 7.4 | 156 | 832 | 0 | 10 | . | 65 | 27 | 3.4 | . | . | . |
| 19 | 11 | 1081 | 95003 | 10.5 | 7.0 | 151 | 780 | 0 | 13 | . | 49 | 33 | 7.3 | . | . | . |
| 20 | 11 | 1081 | 95153 | 10.4 | 7.3 | 153 | 751 | 0 | 12 | . | 43 | 32 | 9.0 | . | . | . |
| 21 | 11 | 1084 | 95023 | 7.9 | 7.0 | 123 | 1003 | 0 | 11 | . | 110 | 31 | 4.6 | . | . | . |
| 22 | 11 | 1084 | 95139 | 9.6 | 7.4 | 159 | 911 | 0 | 12 | . | 84 | 29 | 7.0 | . | . | . |
| 23 | 12 | 1028 | 95076 | 10.1 | 7.2 | 139 | 664 | 0 | 12 | .01 | 27 | 26 | 4.4 | . | . | . |
| 24 | 12 | 1035 | 94119 | 9.7 | 7.0 | 121 | 622 | 0 | 10 | . | . | . | 4.9 | . | . | . |
| 25 | 12 | 1035 | 95076 | 10.4 | 7.3 | 173 | 625 | 0 | 11 | .01 | 16 | 25 | 3.9 | . | . | . |
| 26 | 12 | 1038 | 94147 | 9.5 | 6.7 | 131 | 696 | 0 | 0 | . | . | . | 3.1 | . | . | . |
| 27 | 12 | 1038 | 95111 | 9.1 | 7.4 | 169 | 656 | 0 | 8 | . | 20 | 22 | 3.6 | . | . | . |
| 28 | 12 | 1090 | 95023 | 10.7 | 7.3 | 113 | 411 | 1 | 7 | . | 16 | 23 | . | . | . | . |
| 29 | 12 | 1090 | 95045 | 9.8 | 7.2 | 111 | . | 0 | 8 | . | 16 | 23 | 5.5 | . | . | . |
| 30 | 13 | 1003 | 93322 | 10.6 | 6.7 | -60 | 586 | 0 | 0 | . | 15 | 53 | .9 | . | . | . |
| 31 | 13 | 1003 | 95076 | 10.7 | 7.2 | -48 | 622 | 0 | 0 | .12 | 29 | 55 | 6.3 | . | . | . |
| 32 | 13 | 1082 | 95028 | 9.7 | 7.2 | 120 | 843 | 0 | 2 | . | 34 | 41 | 5.6 | . | . | . |
| 33 | 13 | 1083 | 95028 | 11.4 | 7.2 | 89 | 711 | 0 | 0 | . | 33 | 53 | 4.1 | . | . | . |
| 34 | 13 | 1083 | 95178 | 11.5 | 7.5 | 27 | 855 | 1 | 1 | . | 70 | 47 | 9.5 | . | . | . |
| 35 | 13 | 1108 | 95178 | 10.8 | 7.6 | -64 | 748 | 0 | 0 | . | 42 | 44 | . | . | . | . |
| 36 | 14 | 1002 | 93084 | . | . | . | . | 0 | 20 | . | . | . | . | . | . | . |
| 37 | 14 | 1002 | 93321 | 9.7 | 6.9 | 155 | 556 | 0 | 16 | . | 27 | 20 | 4.5 | . | . | . |
| 38 | 14 | 1002 | 95110 | 8.9 | 7.9 | 127 | 535 | 0 | 15 | . | 29 | 19 | 8.6 | . | . | . |
| 39 | 14 | 1002 | 95179 | 10.5 | 7.6 | 110 | 529 | 0 | 14 | . | 24 | 20 | 2.1 | . | . | . |
| 40 | 14 | 1079 | 95179 | 11.4 | 7.8 | 113 | 486 | 1 | 10 | . | 15 | 23 | 2.3 | . | . | . |
| 41 | 14 | 1088 | 95045 | 10.0 | 7.9 | 116 | . | 0 | 8 | . | 9 | 20 | 6.4 | . | . | . |
| 42 | 14 | 1089 | 95110 | 10.2 | 8.2 | 145 | 354 | 0 | 11 | . | 9 | 18 | 5.7 | . | . | . |
| 43 | 15 | 1102 | 95181 | 11.3 | 7.5 | 128 | 785 | 0 | 6 | . | 64 | 35 | 8.7 | . | . | . |
| 44 | 15 | 1103 | 95103 | 10.8 | 7.3 | 124 | 464 | 0 | 3 | . | 3 | 26 | 4.9 | . | . | . |
| 45 | 16 | 1001 | 93289 | . | . | . | . | 1 | 11 | . | . | . | . | . | . | . |
| 46 | 16 | 1001 | 93322 | 10.6 | 6.9 | 125 | 559 | 1 | 9 | . | 14 | 31 | 3.5 | . | . | . |
| 47 | 16 | 1004 | 93329 | . | . | . | . | 1 | 1 | . | . | . | . | . | . | . |
| 48 | 16 | 1004 | 93330 | . | . | . | . | 1 | 1 | . | . | . | . | . | . | . |
| 49 | 17 | 1006 | 95137 | . | . | . | . | 1 | 11 | . | 13 | 20 | 3.9 | . | . | . |
| 50 | 17 | 1007 | 95137 | . | . | . | . | 0 | 6 | . | 7 | 20 | 3.5 | . | . | . |
| 51 | 17 | 1036 | 95181 | 10.4 | 7.7 | 143 | 690 | 0 | 16 | . | 66 | 18 | 6.6 | . | . | . |
| 52 | 17 | 1039 | 95145 | 9.9 | 7.3 | 154 | 1128 | 1 | 13 | . | 112 | 23 | 6.4 | . | . | . |
| 53 | 18 | 1005 | 93033 | 10.0 | 7.6 | 233 | 769 | 0 | 16 | .00 | 36 | 31 | . | . | . | . |
| 54 | 18 | 1005 | 95139 | 10.4 | 7.6 | 154 | 759 | 0 | 18 | . | 32 | 27 | 3.2 | . | . | . |
| 55 | 18 | 1050 | 95103 | 8.8 | 7.3 | 128 | 867 | 0 | 11 | . | 44 | 27 | 2.9 | . | . | . |
| 56 | 18 | 1058 | 95171 | 10.3 | 7.3 | 141 | 1078 | 1 | 22 | . | 44 | 26 | 2.2 | . | . | . |
| 57 | 18 | 1085 | 95181 | 10.9 | 7.7 | 130 | 576 | 0 | 9 | . | 17 | 28 | . | . | . | . |
| 58 | 18 | 1086 | 95181 | 11.0 | 7.7 | 132 | 586 | . | . | . | . | [illegible] | . | . | . | . |



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| | cc | site | date | temp | ph | eh | cond | bac | no | nh | cl | so | obi | x | y | z |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 59 | 18 | 1087 | 95181 | 10.2 | 7.3 | 124 | 946 | 1 | 23 | . | 43 | 39 | 2.7 | . | . | . |
| 60 | 19 | 1047 | 95152 | 10.6 | 7.5 | 129 | 679 | 1 | 1 | . | 27 | 40 | 3.5 | . | . | . |
| 61 | 19 | 1048 | 95171 | 10.8 | 7.4 | 144 | 758 | 0 | 6 | . | 36 | 32 | 1.8 | . | . | . |
| 62 | 19 | 1049 | 95171 | 10.7 | 7.6 | 140 | 642 | 1 | 3 | . | 20 | 38 | 3.8 | . | . | . |
| 63 | 19 | 1052 | 95152 | 10.7 | 7.4 | 140 | 743 | 0 | 5 | . | 34 | 42 | 5.3 | . | . | . |
| 64 | 31 | 3017 | 95024 | 10.7 | 7.1 | 119 | 588 | 1 | 1 | . | 8 | 50 | 5.1 | . | . | . |
| 65 | 31 | 3072 | 95024 | 7.6 | 7.5 | 119 | 632 | 0 | 4 | . | 11 | 40 | 8.9 | . | . | . |
| 66 | 31 | 3073 | 95053 | 8.5 | 7.3 | 138 | 852 | 1 | 6 | . | 64 | 18 | 7.2 | . | . | . |
| 67 | 31 | 3073 | 95147 | 8.6 | 7.4 | 169 | 667 | 1 | 5 | . | 13 | 17 | . | . | . | . |
| 68 | 31 | 3109 | 95180 | 11.9 | 7.4 | 114 | 574 | 1 | 9 | . | 12 | 16 | . | . | . | . |
| 69 | 32 | 3104 | 95146 | 9.7 | 7.7 | 173 | 598 | 0 | 9 | . | 9 | 14 | . | . | . | . |
| 70 | 32 | 3105 | 95147 | 10.1 | 7.2 | 149 | 1156 | 0 | 12 | . | 117 | 25 | 1.9 | . | . | . |
| 71 | 32 | 3106 | 95154 | 10.0 | 7.3 | 198 | 619 | 1 | 6 | . | 8 | 17 | 2.0 | . | . | . |
| 72 | 34 | 3056 | 95175 | 17.4 | 7.7 | 130 | 626 | . | . | . | . | . | 2.5 | . | . | . |
| 73 | 35 | 3057 | 95173 | 8.6 | 7.2 | 160 | 692 | 1 | 5 | . | 16 | 17 | 1.7 | . | . | . |
| 74 | 35 | 3067 | 95173 | 9.6 | 7.3 | 147 | 609 | 1 | 8 | . | 17 | 19 | . | . | . | . |
| 75 | 35 | 3068 | 95173 | 9.8 | 7.3 | 150 | 692 | 1 | 8 | . | 18 | 18 | . | . | . | . |
| 76 | 35 | 3070 | 95173 | 10.0 | 7.2 | 150 | 703 | 1 | 23 | . | 30 | 27 | . | . | . | . |
| 77 | 40 | 4040 | 94147 | 10.6 | 6.3 | 149 | 1198 | 1 | 1 | . | . | . | 3.1 | . | . | . |
| 78 | 40 | 4040 | 95174 | 11.5 | 7.1 | 155 | 1316 | 1 | 10 | . | 135 | 31 | 5.3 | . | . | . |
| 79 | 40 | 4041 | 95145 | 9.1 | 7.1 | 149 | 1039 | 1 | 20 | . | 49 | 20 | 6.1 | . | . | . |
| 80 | 40 | 4091 | 95174 | 11.9 | 7.3 | 150 | 877 | 0 | 12 | . | 36 | 22 | . | . | . | . |
| 81 | 50 | 5062 | 95175 | 16.1 | 7.9 | 479 | 549 | . | . | . | . | . | 5.7 | . | . | . |
| 82 | 70 | 7078 | 95053 | 9.0 | 6.9 | 160 | 702 | 1 | 7 | . | 43 | 20 | 3.4 | . | . | . |
| 83 | 70 | 7078 | 95145 | 10.2 | 7.2 | 152 | 656 | 1 | 6 | . | 25 | 17 | 1.7 | . | . | . |
| 84 | 70 | 7092 | 95052 | 10.1 | 7.1 | 133 | 677 | 0 | 6 | . | 27 | 30 | 5.0 | . | . | . |
| 85 | 70 | 7092 | 95145 | 9.5 | 7.3 | 155 | 681 | 0 | 6 | . | 28 | 28 | 1.7 | . | . | . |
| 86 | 70 | 7093 | 95053 | 9.4 | 6.9 | 160 | 682 | 0 | 5 | . | 17 | 21 | 5.7 | . | . | . |
| 87 | 70 | 7093 | 95145 | 9.5 | 7.1 | 159 | 677 | 0 | 6 | . | 20 | 19 | 2.9 | . | . | . |





| | cc | site | date | temp | ph | eh | cond | bac | no | nh | cl | so | obi | x | y | z |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 88 | 71 | 7074 | 95029 | 9.4 | 6.9 | 101 | 966 | 1 | 2 | . | 70 | 34 | . | . | . | . |
| 89 | 71 | 7074 | 95052 | 9.0 | 6.9 | 85 | 762 | 0 | 2 | . | 85 | 32 | 4.8 | . | . | . |
| 90 | 71 | 7074 | 95144 | 9.4 | 7.2 | 113 | 943 | 1 | 2 | . | 88 | 35 | 7.7 | . | . | . |
| 91 | 71 | 7075 | 95052 | 13.1 | 7.1 | 119 | 736 | 0 | 1 | . | 46 | 25 | 5.3 | . | . | . |
| 92 | 71 | 7075 | 95144 | 10.5 | 7.2 | 106 | 786 | 0 | 1 | . | 49 | 27 | 4.8 | . | . | . |
| 93 | 71 | 7076 | 95052 | 9.5 | 6.8 | 137 | 1114 | 0 | 11 | . | 106 | 53 | 5.6 | . | . | . |
| 94 | 71 | 7076 | 95144 | 9.6 | 7.2 | 148 | 1267 | 0 | 9 | . | 137 | 67 | 5.7 | . | . | . |
| 95 | 71 | 7077 | 95052 | 9.3 | 6.9 | 137 | 990 | 0 | 6 | . | 84 | 45 | 5.1 | . | . | . |
| 96 | 71 | 7077 | 95144 | 10.0 | 7.2 | 153 | 991 | 0 | 7 | . | 77 | 42 | . | . | . | . |
| 97 | 71 | 7094 | 95144 | 9.3 | 7.1 | 141 | 1009 | 0 | 8 | . | 60 | 39 | 4.9 | . | . | . |
| 98 | 72 | 7095 | 95143 | 9.6 | 7.3 | 62 | 757 | 1 | 0 | . | 25 | 39 | 5.4 | . | . | . |
| 99 | 72 | 7095 | 95168 | . | . | . | . | 0 | 0 | . | 24 | 40 | 1.6 | . | . | . |
| 100 | 72 | 7096 | 95168 | . | . | . | . | 0 | 0 | . | 15 | 43 | 2.6 | . | . | . |
| 101 | 72 | 7097 | 95168 | . | . | . | . | 1 | 0 | . | 5 | 15 | 7.3 | . | . | . |
| 102 | 80 | 8053 | 95138 | . | . | . | . | 1 | 5 | . | 8 | 11 | 2.1 | . | . | . |
| 103 | 80 | 8054 | 95138 | . | . | . | . | 0 | 4 | . | 7 | 11 | 2.2 | . | . | . |
| 104 | 90 | 9098 | 95172 | 10.1 | 7.5 | 152 | 581 | 0 | 5 | . | 10 | 20 | 5.7 | . | . | . |
| 105 | 90 | 9099 | 95172 | 9.9 | 7.5 | 160 | 657 | 1 | 6 | . | 29 | 21 | . | . | . | . |
| 106 | 90 | 9107 | 95172 | 8.0 | 7.5 | 177 | 661 | 1 | 6 | . | 23 | 20 | . | . | . | . |

TABLE 3. SELECTED ANALYTICAL DATA SORTED BY SAMPLE SITE



| | cc | site | date | temp | ph | eh | cond | b | no | nh | cl | so | obi | x | y | z |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 16 | 1001 | 93289 | . | . | . | . | 1 | 11 | . | . | . | . | . | . | . |
| 2 | 16 | 1001 | 93322 | 10.6 | 6.9 | 125 | 559 | 1 | 9 | . | 14 | 31 | 3.5 | . | . | . |
| 3 | 14 | 1002 | 93084 | . | . | . | . | 0 | 20 | . | . | . | . | . | . | . |
| 4 | 14 | 1002 | 93321 | 9.7 | 6.9 | 155 | 556 | 0 | 16 | . | 27 | 20 | 4.5 | . | . | . |
| 5 | 14 | 1002 | 95110 | 8.9 | 7.9 | 127 | 535 | 0 | 15 | . | 29 | 19 | 8.6 | . | . | . |
| 6 | 14 | 1002 | 95179 | 10.5 | 7.6 | 110 | 529 | 0 | 14 | . | 24 | 20 | 2.1 | . | . | . |
| 7 | 13 | 1003 | 93322 | 10.6 | 6.7 | -60 | 586 | 0 | 0 | . | 15 | 53 | .9 | . | . | . |
| 8 | 13 | 1003 | 95076 | 10.7 | 7.2 | -48 | 622 | 0 | 0 | .12 | 29 | 55 | 6.3 | . | . | . |
| 9 | 16 | 1004 | 93329 | . | . | . | . | 1 | 1 | . | . | . | . | . | . | . |
| 10 | 16 | 1004 | 93330 | . | . | . | . | 1 | 1 | . | . | . | . | . | . | . |
| 11 | 18 | 1005 | 93033 | 10.0 | 7.6 | 233 | 769 | 0 | 16 | .00 | 36 | 31 | . | . | . | . |
| 12 | 18 | 1005 | 95139 | 10.4 | 7.6 | 154 | 759 | 0 | 18 | . | 32 | 27 | 3.2 | . | . | . |
| 13 | 17 | 1006 | 95137 | . | . | . | . | 1 | 11 | . | 13 | 20 | 3.9 | . | . | . |
| 14 | 17 | 1007 | 95137 | . | . | . | . | 0 | 6 | . | 7 | 20 | 3.5 | . | . | . |
| 15 | 31 | 3017 | 95024 | 10.7 | 7.1 | 119 | 588 | 1 | 1 | . | 8 | 50 | 5.1 | . | . | . |
| 16 | 10 | 1021 | 95165 | 10.2 | 7.2 | 147 | 978 | 0 | 12 | . | 88 | 34 | 22.0 | . | . | . |
| 17 | 10 | 1026 | 95165 | 10.7 | 7.1 | 152 | 1056 | 0 | 11 | . | 98 | 45 | 6.3 | . | . | . |
| 18 | 12 | 1028 | 95076 | 10.1 | 7.2 | 139 | 664 | 0 | 12 | .01 | 27 | 26 | 4.4 | . | . | . |
| 19 | 11 | 1029 | 94010 | . | . | . | . | 0 | 13 | . | . | . | 2.0 | . | . | . |
| 20 | 11 | 1029 | 95002 | 9.4 | 7.1 | 164 | 966 | 0 | 12 | . | 92 | 32 | 7.1 | . | . | . |
| 21 | 11 | 1030 | 94083 | . | . | . | . | 0 | 20 | . | . | . | 1.7 | . | . | . |
| 22 | 11 | 1030 | 95140 | 9.8 | 7.5 | 165 | 777 | 0 | 22 | . | 21 | 35 | 2.4 | . | . | . |
| 23 | 11 | 1031 | 94083 | . | . | . | . | 0 | 20 | . | . | . | 2.8 | . | . | . |
| 24 | 11 | 1031 | 95111 | 9.4 | 7.4 | 151 | 781 | 0 | 22 | . | 32 | 39 | 5.8 | . | . | . |
| 25 | 11 | 1034 | 94119 | . | . | . | . | 1 | 8 | . | . | . | 3.3 | . | . | . |
| 26 | 11 | 1034 | 95104 | 9.4 | 7.7 | 166 | 602 | 1 | 7 | . | 14 | 28 | 5.5 | . | . | . |
| 27 | 11 | 1034 | 95181 | 10.3 | 7.6 | 123 | 426 | 1 | 7 | . | 12 | 27 | 4.0 | . | . | . |
| 28 | 12 | 1035 | 94119 | 9.7 | 7.0 | 121 | 622 | 0 | 10 | . | . | . | 4.9 | . | . | . |
| 29 | 12 | 1035 | 95076 | 10.4 | 7.3 | 173 | 625 | 0 | 11 | .01 | 16 | 25 | 2.0 | . | . | . |





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| 30 | 17 | 1036 | 95181 | 10.4 | 7.7 | 143 | 690 | 0 | 16 | . | 66 | 18 | 6.6 | . | . | . |
| 31 | 11 | 1037 | 94147 | 11.9 | 6.5 | 124 | 1201 | 0 | 7 | . | . | . | 2.9 | . | . | . |
| 32 | 11 | 1037 | 95152 | 10.9 | 7.3 | 149 | 1165 | 0 | 8 | . | 139 | 31 | 6.2 | . | . | . |
| 33 | 12 | 1038 | 94147 | 9.5 | 6.7 | 131 | 696 | 0 | 0 | . | . | . | 3.1 | . | . | . |
| 34 | 12 | 1038 | 95111 | 9.1 | 7.4 | 169 | 656 | 0 | 8 | . | 20 | 22 | 3.6 | . | . | . |
| 35 | 17 | 1039 | 95145 | 9.9 | 7.3 | 154 | 1128 | 1 | 13 | . | 112 | 23 | 6.4 | . | . | . |
| 36 | 40 | 4040 | 94147 | 10.6 | 6.3 | 149 | 1198 | 1 | 1 | . | . | . | 3.1 | . | . | . |
| 37 | 40 | 4040 | 95174 | 11.5 | 7.1 | 155 | 1316 | 1 | 10 | . | 135 | 31 | 5.3 | . | . | . |
| 38 | 40 | 4041 | 95145 | 9.1 | 7.1 | 149 | 1039 | 1 | 20 | . | 49 | 20 | 6.1 | . | . | . |
| 39 | 19 | 1047 | 95152 | 10.6 | 7.5 | 129 | 679 | 1 | 1 | . | 27 | 40 | 3.5 | . | . | . |
| 40 | 19 | 1048 | 95171 | 10.8 | 7.4 | 144 | 758 | 0 | 6 | . | 36 | 32 | 1.8 | . | . | . |
| 41 | 19 | 1049 | 95171 | 10.7 | 7.6 | 140 | 642 | 1 | 3 | . | 20 | 38 | 3.8 | . | . | . |
| 42 | 18 | 1050 | 95103 | 8.8 | 7.3 | 128 | 867 | 0 | 11 | . | 44 | 27 | 2.9 | . | . | . |
| 43 | 10 | 1051 | 95166 | 10.1 | 7.3 | 137 | 1962 | 1 | 13 | . | 344 | 49 | 4.5 | . | . | . |
| 44 | 19 | 1052 | 95152 | 10.7 | 7.4 | 140 | 743 | 0 | 5 | . | 34 | 42 | 5.3 | . | . | . |
| 45 | 80 | 8053 | 95138 | . | . | . | . | 1 | 5 | . | 8 | 11 | 2.1 | . | . | . |
| 46 | 80 | 8054 | 95138 | . | . | . | . | 0 | 4 | . | 7 | 11 | 2.2 | . | . | . |
| 47 | 34 | 3056 | 95175 | 17.4 | 7.7 | 130 | 626 | . | . | . | . | . | 2.5 | . | . | . |
| 48 | 35 | 3057 | 95173 | 8.6 | 7.2 | 160 | 692 | 1 | 5 | . | 16 | 17 | 1.7 | . | . | . |
| 49 | 18 | 1058 | 95171 | 10.3 | 7.3 | 141 | 1078 | 1 | 22 | . | 44 | 26 | 2.2 | . | . | . |
| 50 | 50 | 5062 | 95175 | 16.1 | 7.9 | 479 | 549 | . | . | . | . | . | 5.7 | . | . | . |
| 51 | 35 | 3067 | 95173 | 9.6 | 7.3 | 147 | 609 | 1 | 8 | . | 17 | 19 | . | . | . | . |
| 52 | 35 | 3068 | 95173 | 9.8 | 7.3 | 150 | 692 | 1 | 8 | . | 18 | 18 | . | . | . | . |
| 53 | 11 | 1069 | 95003 | 10.5 | 7.1 | 138 | 838 | 0 | 10 | . | 67 | 31 | 4.0 | . | . | . |
| 54 | 11 | 1069 | 95153 | 10.9 | 7.5 | 159 | 793 | 0 | 10 | . | 58 | 30 | 5.4 | . | . | . |
| 55 | 35 | 3070 | 95173 | 10.0 | 7.2 | 150 | 703 | 1 | 23 | . | 30 | 27 | . | . | . | . |
| 56 | 31 | 3072 | 95024 | 7.6 | 7.5 | 119 | 632 | 0 | 4 | . | 11 | 40 | 8.9 | . | . | . |
| 57 | 31 | 3073 | 95053 | 8.5 | 7.3 | 138 | 852 | 1 | 6 | . | 64 | 18 | 7.2 | . | . | . |
| 58 | 31 | 3073 | 95147 | 8.6 | 7.4 | 169 | 667 | 1 | 5 | . | 13 | 17 | . | . | . | . |

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| 59 | 71 | 7074 | 95029 | 9.4 | 6.9 | 101 | 966 | 1 | 2 | . | 70 | 34 | . | . | . | . |
| 60 | 71 | 7074 | 95052 | 9.0 | 6.9 | 85 | 762 | 0 | 2 | . | 85 | 32 | 4.8 | . | . | . |
| 61 | 71 | 7074 | 95144 | 9.4 | 7.2 | 113 | 943 | 1 | 2 | . | 88 | 35 | 7.7 | . | . | . |
| 62 | 71 | 7075 | 95052 | 13.1 | 7.1 | 119 | 736 | 0 | 1 | . | 46 | 25 | 5.3 | . | . | . |
| 63 | 71 | 7075 | 95144 | 10.5 | 7.2 | 106 | 786 | 0 | 1 | . | 49 | 27 | 4.8 | . | . | . |
| 64 | 71 | 7076 | 95052 | 9.5 | 6.8 | 137 | 1114 | 0 | 11 | . | 106 | 53 | 5.6 | . | . | . |
| 65 | 71 | 7076 | 95144 | 9.6 | 7.2 | 148 | 1267 | 0 | 9 | . | 137 | 67 | 5.7 | . | . | . |
| 66 | 71 | 7077 | 95052 | 9.3 | 6.9 | 137 | 990 | 0 | 6 | . | 84 | 45 | 5.1 | . | . | . |
| 67 | 71 | 7077 | 95144 | 10.0 | 7.2 | 153 | 991 | 0 | 7 | . | 77 | 42 | . | . | . | . |
| 68 | 70 | 7078 | 95053 | 9.0 | 6.9 | 160 | 702 | 1 | 7 | . | 43 | 20 | 3.4 | . | . | . |
| 69 | 70 | 7078 | 95145 | 10.2 | 7.2 | 152 | 656 | 1 | 6 | . | 25 | 17 | 1.7 | . | . | . |
| 70 | 14 | 1079 | 95179 | 11.4 | 7.8 | 113 | 486 | 1 | 10 | . | 15 | 23 | 2.3 | . | . | . |
| 71 | 11 | 1080 | 95002 | 10.0 | 7.1 | 140 | 838 | 0 | 10 | . | 68 | 28 | 5.5 | . | . | . |
| 72 | 11 | 1080 | 95139 | 10.4 | 7.4 | 156 | 832 | 0 | 10 | . | 65 | 27 | 3.4 | . | . | . |
| 73 | 11 | 1081 | 95003 | 10.5 | 7.0 | 151 | 780 | 0 | 13 | . | 49 | 33 | 7.3 | . | . | . |
| 74 | 11 | 1081 | 95153 | 10.4 | 7.3 | 153 | 751 | 0 | 12 | . | 43 | 32 | 9.0 | . | . | . |
| 75 | 13 | 1082 | 95028 | 9.7 | 7.2 | 120 | 843 | 0 | 2 | . | 34 | 41 | 5.6 | . | . | . |
| 76 | 13 | 1083 | 95028 | 11.4 | 7.2 | 89 | 711 | 0 | 0 | . | 33 | 53 | 4.1 | . | . | . |
| 77 | 13 | 1083 | 95178 | 11.5 | 7.5 | 27 | 855 | 1 | 1 | . | 70 | 47 | 9.5 | . | . | . |
| 78 | 11 | 1084 | 95023 | 7.9 | 7.0 | 123 | 1003 | 0 | 11 | . | 110 | 31 | 4.6 | . | . | . |
| 79 | 11 | 1084 | 95139 | 9.6 | 7.4 | 159 | 911 | 0 | 12 | . | 84 | 29 | 7.0 | . | . | . |
| 80 | 18 | 1085 | 95181 | 10.9 | 7.7 | 130 | 576 | 0 | 9 | . | 17 | 28 | . | . | . | . |
| 81 | 18 | 1086 | 95181 | 11.0 | 7.7 | 132 | 586 | . | . | . | . | . | . | . | . | . |
| 82 | 18 | 1087 | 95181 | 10.2 | 7.3 | 124 | 946 | 1 | 23 | . | 43 | 39 | 2.7 | . | . | . |
| 83 | 14 | 1088 | 95045 | 10.0 | 7.9 | 116 | . | 0 | 8 | . | 9 | 20 | 6.4 | . | . | . |
| 84 | 14 | 1089 | 95110 | 10.2 | 8.2 | 145 | 354 | 0 | 11 | . | 9 | 18 | 5.7 | . | . | . |
| 85 | 12 | 1090 | 95023 | 10.7 | 7.3 | 113 | 411 | 1 | 7 | . | 16 | 23 | . | . | . | . |
| 86 | 12 | 1090 | 95045 | 9.8 | 7.2 | 111 | . | 0 | 8 | . | 16 | 23 | 5.5 | . | . | . |
| 87 | 40 | 4091 | 95174 | 11.9 | 7.3 | 150 | 877 | 0 | 12 | . | 36 | 22 | . | . | . | . |





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| 88 | 70 | 7092 | 95052 | 10.1 | 7.1 | 133 | 677 | 0 | 6 | . | 27 | 30 | 5.0 | . | . | . |
| 89 | 70 | 7092 | 95145 | 9.5 | 7.3 | 155 | 681 | 0 | 6 | . | 28 | 28 | 1.7 | . | . | . |
| 90 | 70 | 7093 | 95053 | 9.4 | 6.9 | 160 | 682 | 0 | 5 | . | 17 | 21 | 5.7 | . | . | . |
| 91 | 70 | 7093 | 95145 | 9.5 | 7.1 | 159 | 677 | 0 | 6 | . | 20 | 19 | 2.9 | . | . | . |
| 92 | 71 | 7094 | 95144 | 9.3 | 7.1 | 141 | 1009 | 0 | 8 | . | 60 | 39 | 4.9 | . | . | . |
| 93 | 72 | 7095 | 95143 | 9.6 | 7.3 | 62 | 757 | 1 | 0 | . | 25 | 39 | 5.4 | . | . | . |
| 94 | 72 | 7095 | 95168 | . | . | . | . | 0 | 0 | . | 24 | 40 | 1.6 | . | . | . |
| 95 | 72 | 7096 | 95168 | . | . | . | . | 0 | 0 | . | 15 | 43 | 2.6 | . | . | . |
| 96 | 72 | 7097 | 95168 | . | . | . | . | 1 | 0 | . | 5 | 15 | 7.3 | . | . | . |
| 97 | 90 | 9098 | 95172 | 10.1 | 7.5 | 152 | 581 | 0 | 5 | . | 10 | 20 | 5.7 | . | . | . |
| 98 | 90 | 9099 | 95172 | 9.9 | 7.5 | 160 | 657 | 1 | 6 | . | 29 | 21 | . | . | . | . |
| 99 | 15 | 1102 | 95181 | 11.3 | 7.5 | 128 | 785 | 0 | 6 | . | 64 | 35 | 8.7 | . | . | . |
| 100 | 15 | 1103 | 95103 | 10.8 | 7.3 | 124 | 464 | 0 | 3 | . | 3 | 26 | 4.9 | . | . | . |
| 101 | 32 | 3104 | 95146 | 9.7 | 7.7 | 173 | 598 | 0 | 9 | . | 9 | 14 | . | . | . | . |
| 102 | 32 | 3105 | 95147 | 10.1 | 7.2 | 149 | 1156 | 0 | 12 | . | 117 | 25 | 1.9 | . | . | . |
| 103 | 32 | 3106 | 95154 | 10.0 | 7.3 | 198 | 619 | 1 | 6 | . | 8 | 17 | 2.0 | . | . | . |
| 104 | 90 | 9107 | 95172 | 8.0 | 7.5 | 177 | 661 | 1 | 6 | . | 23 | 20 | . | . | . | . |
| 105 | 13 | 1108 | 95178 | 10.8 | 7.6 | -64 | 748 | 0 | 0 | . | 42 | 44 | . | . | . | . |
| 106 | 31 | 3109 | 95180 | 11.9 | 7.4 | 114 | 574 | 1 | 9 | . | 12 | 16 | . | . | . | . |

ATTACHMENT 2.

# OPTICAL BRIGHTENER SCREENING FOR SEWAGE CONTAMINATION OF WATER TABLE AQUIFERS IN SOUTHEASTERN MINNESOTA, USA

Ronald C. Spong[1], Steffan R. Fay[2] and E. Calvin Alexander, Jr.[2]


## ABSTRACT

Novel screening methods for detecting optical brighteners, fluorescent organic blue dyes principally used in laundry detergents for whitening fabrics, have been developed for the monitoring of water table aquifers impacted by septic systems. Four rural residential communities characterized by private water supply and sewage systems were selected in southeastern Minnesota. Developments were chosen with a variety of saturated and unsaturated zone materials and thicknesses, water table and well depths, and topographic and cultural settings. Sampling sites were enrolled if wells were completed above regional aquitards. Sanitary surveys of sampling sites were completed with attention to drinking water usage and waste/wastewater disposal practices to uncover sources of cross-contamination. Water supplies were sampled and analyzed to determine aquifer sources, sanitary quality and natural backgrounds and anthropomorphic contributions of physicochemical and microbiological parameters of interest (e.g., nitrate, chloride and coliform bacteria). Filter holders containing untreated cotton, activated carbon and polysulfone/polyethersulfone membrane filters were installed as immersion-type detectors in toilet reservoirs. Syringe filter capsules comprised of polyethersulfone membranes were utilized for direct sampling. Exposure times ranged from minutes to months, and exposed filter media were analyzed in solid phase utilizing a scanning spectrofluorophotometer. Spectral data were computer-processed to objectively match peaks with the spectra obtained from pure fluorescent dyes and laundry detergent formulations. Detections were positive if matched peaks at 440 nm appeared above background fluorescence. Water supply test data and site survey information indicative of septic system contamination were moderately correlated with positive optical brightener detections.



## KEY WORDS

Fluorescent whitening agents (FWA) or optical brighteners; groundwater contamination; septic systems or on-site sewage systems; and water table aquifers.


## INTRODUCTION

Septic systems and other waste and wastewater disposal practices account for a significant share of the nonpoint source pollution that directly and indirectly impacts the burgeoning rural and urban unsewered communities in Minnesota which are largely dependent on groundwater resources for drinking water supplies (MPCA, 1989). Many quantitative contaminants, such as nitrate which has a natural background concentration less than 1.0 mg N/L in regional groundwaters, have potentially several sources. Therefore, it is difficult to assign responsibility for the impacts, target timely and effective remediation and facilitate land use planning and education to prevent and mitigate the pollution. This is especially true in agricultural settings where, for example, nitrogen from fertilizers and livestock operations is practically indistinguishable from septic system nitrogen.

Traditional sanitary indicators of drinking water supplies, such as coliform bacteria and nitrate, are ambiguous, especially if test results are variable, at or below background levels or negative. Straining, adsorption and competition limit fecal bacteria migration and survival, and reducing or denitrifying conditions either slow nitrogen oxidation to nitrate or reverse it (Bitton and Gerba, 1984). Negative sanitary tests alone do not prove that a water supply is safe for human consumption without more extensive testing. Other quantitative pollution parameters indicative of septic system contamination, including electrical or specific conductance and chloride, give similar equivocal results. Therefore, septic system-specific, qualitative contaminants (i.e., with no natural background concentrations in groundwaters), such as surfactants (MBAS - methylene blue active substances, etc.) and optical brighteners, also known as fluorescent whitening agents (FWA), have been investigated as septic system indicators.

Synthethic optical brighteners were developed in the 1930's by organic chemists after Krais in 1929 isolated aesculin (a glucosidal derivative of coumarin) from horse chestnuts which temporarily brightened linen (Zahradnik, 1982). Following World War II, additional optical brighteners, derived from DASC (diaminostilbene/cyanuric chloride), DSBP (distyrylbiphenyl) and other aromatic hydrocarbons, were synthesized and found widespread commercial application. Use in detergent compounds for whitening fabrics, especially cotton, accounts for approximately 80 percent of the optical brighteners produced annually in the United States.


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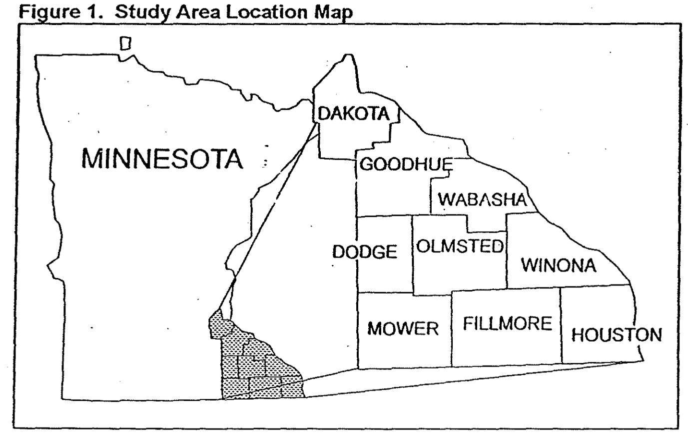
Optical brighteners comprise between 0.1 and 2 percent by weight of modern laundry product formulations (average range of 0.2-0.5 percent). In Minnesota, non-commercial phosphate detergents were banned in 1970 to slow the progressive eutrophication of the State's valuable recreational surface water resources. Synthetic detergent compounds, such as linear alkyl sulfonates, were substituted but first met with dissatisfaction because of "dingy", "dull" looking, washed clothing. Manufacturers responded by adding higher concentrations of optical brighteners to enhance the appearance. Consequently, optical brighteners have been discharged to septic systems for 25 years and have been detected in surface and ground waters in southeastern Minnesota (Spong, 1993).

Since the mid-1970's, interest in optical brighteners or fluorescent whitening agents (FWA) as passive tracers of septic system contamination of groundwaters has been pursued by researchers with varied results. Kerfoot and Brainard (1978) recommended optical brighteners as indicators of septic system pollution which eventually led to the commercial development of instruments known as "Septic Leachate Detectors" or "Septic Snoopers". The instruments combined a filter fluorometer with a specific conductivity meter and were used in Clean Water Act-funded lake pollution and restoration studies in the late 1970's through the mid-1980's. However, their reliability and specificity were debated when studies of fluorescent, dissolved organic carbon compounds (FDOC), including natural humic and fulvic acids, suggested significant interferences (Carlson and Shapiro, 1981).

Alhajjar, et al (1990) reported in a study of seventeen residential septic systems in central Wisconsin that optical brighteners were unsatisfactory as indicators of shallow aquifer sewage contamination. Utilizing upgradient and downgradient drivepoints for sampling and filter fluorometry for FWA analysis of aqueous samples, they reasoned that the undetectable optical brighteners were decomposing or sorbing to soil. They found that dissolved solids (detected as specific conductance) moved through the soil, and chloride was cited as the most reliable sewage indicator. However, use of non-chlorine bleach-stable DASC optical brighteners, well placement and sampling, aqueous sample filter fluorometry and FDOC interference may account for the lack of FWA detections.

Optical brighteners are reliable tracers in karst hydrogeologic investigations despite FDOC interefences and dye costs (Smart and Laidlaw, 1977; Aley, 1985; Alexander and Quinlan, 1992). Fay, et al, (this publication) describe the use of scanning spectrofluorophotometry for solid phase detection of optical brighteners and other fluorescent dyes. Such advances in selective filter media adsorption, fluorometric technology and procedures and the computer processing of resulting spectral data address concerns of low and variable optical brightener concentrations, interfering background fluoresence and subjective data evaluation appearing in the literature.

Figure 1. Study Area Location Map




## METHODS AND MATERIALS

### *Site Selection, Evaluation and Sampling*

This Minnesota Legislature-approved research project (Spong, 1993) encompasses a nine-county area of southeastern Minnesota (Figure 1.), and the four communities selected represent a variety of cultural, topographic and hydrogeologic settings (Table 1.) with which to test the hypothesis that optical brighteners selectively sorbed to cotton, other cellulosic fibers and selective filter media can be reliable qualitative and, perhaps, semi-quantitative indicators of septic system contamination of groundwaters. The villages of Castle Rock, Coates, Empire City and Vasa are rural residential communities comprised of urban laborers and local agribusiness, service industry and retired persons. All are characterized by early 1900's structures, limited road and drainage improvements and pre-Code wells and septic systems. New buildings, wells, septic systems and other enhancements occur infrequently.

Older residences were chosen for the project primarily because they were served by wells completed in surficial, unconfined aquifers above regional aquitards. Participation in the project was voluntary and required access for sampling and a brief survey. An average of 75 percent of those solicited declined to participate which limited site selection in most communities. Once selected, participants were interviewed about a number of residential living habits, knowledge of their wells, septic systems and other practices, general health and concerns. Sanitary surveys were conducted of the wells and water supplies, septic systems and other waste and wastewater disposal devices with particular attention to potential cross-contamination.

Filter holders were secured in the reservoirs of the most used toilet in buildings, and water supplies were sampled and analyzed in the field and laboratory. Owners were apprised of test results and any recommendations if problems were observed. Filter holders were retrieved and replaced periodically, and water supplies were resampled to help resolve certain problems (e.g., coliform bacteria present).

**Table 1. Cultural, Topographic, Geomorphic and Hydrogeologic Features of Four Communities**

| Feature | Castle Rock | Coates | Empire City | Vasa |
|---|---|---|---|---|
| County (area) | Dakota (southwest) | Dakota (north) | Dakota (central) | Goodhue (north) |
| Occupied Buildings | 67(7 nonresidential) | 62(5 nonresidential) | 57(2 nonresidential) | 43(7 nonresidential) |
| Polygonal Area | 121 ha (299 acres) | 65 ha (160 acres) | 19 ha (47 acres) | 53 ha (130 acres) |
| Vertical Relief | 9 m (29.5 ft) | 7 m (23 ft) | 4 m (13 ft) | 21 m (69 ft) |
| Slope (% gradient) | 0% ~ 6% | 1% ~ 6% | 0% ~ 2% | 2% ~ 12% |
| Soils | loam, silty loam (cl) | silty to sandy loam | loam to loamy sand | silty loam to loam |
| Geomorphology | pre-Qw morraine - outwash plain | loess-mantled Qw outwash plain | buried bdrk valley alluvial/Qw outwash | loess-mantled pre-Qw till |
| Surficial Bedrock | rsdl ss, dolostone | rsdl ss, dolostone | dolostone | rsdl ss, dolostone |
| Bedrock Depth | 3-14 m (9-46 ft) | 15-27 m (50-90 ft) | 3-91m (10-300 ft) | 1-15 m (3-50 ft) |
| Water Table Depth | 3-12 m (10-40 ft) | 21-27 m (70-90 ft) | 3-12 m (10-40 ft) | 12-18 m (40-60 ft) |
| Shallow Well Depth | Drivepoints 6-9 m Drilled wells 12-55m | Drilled wells 21-61m | Drivepoints 6-9 m Drilled wells 12-46m | Drilled wells 18-76m |
| Shallow Aquifer Flow | East-southeast | Northeast | Northeast | North-northeast |

*NB: ha = hectares; m = meters; ft = feet; cl = clay loam; Qw = Wisconsinan; rsdl ss = residual sandstone*

***Optical Brightener Filter Media, Sampling and Analysis***

Immersion filter holders were constructed of fine-mesh, black fiberglas window screening which was distilled water-rinsed, folded and stapled to form separate compartments for the filter media and channels for plastic tywraps that were used to secure filter holders to the toilets' standpipes. Filter media included untreated cotton facial pads (Target and Johnson & Johnson brands), activated carbon (Fisher Scientific: 6-14 mesh) and polysulfone/polyethersulfone 0.45 um-pore membrane filters (Gelman Science: trademarks "Tuffryn", "Supor", "Biotrace" and "UltraBind"). Precautions were taken to isolate the filter media and holder materials from possible optical brightener contamination. Completed holders and filter media were tracked as lots, randomly sampled and analyzed as "blanks" to control for false positives. If a blank tested positive, the entire lot was discarded.

In place of direct aqueous samples where FDOC interference significantly limits detection of very low optical brightener concentrations in groundwaters, cotton was selected due to its success in karst water tracing studies (Aley, 1985; Alexander and Quinlan, 1992). Side-by-side comparisons were run with cotton and activated carbon, the latter being a non-selective FDOC adsorption medium. Cotton was found to be largely uneffected by FDOC adsorption. However, solid phase fluorometric analysis of cotton blanks consistently found a characteristic peak (emission wavelength of 414 nm) which could interfere with sample analysis. Cotton blank reference spectra were then used for background comparisons. Also, some cotton products were excluded from use as they were found to contain traces of optical brighteners likely from the inclusion of recycled, formerly brightened cotton.

Laboratory trials with syringe filter capsules (Gelman Science: trademark "Acrodisc" and "Acrodisc PF"), in which 0.2 um-pore polyethersulfone membrane filters preferentially sorbed optical brighteners (Fay, et al, this publication) during column experiments, was followed by field sampling utilizing disposable syringe and peristaltic and manual vacuum pump collection methods. Insufficient data precludes reporting at this time.

Solid phase fluorometry was performed at the University of Minnesota Hydrogeochemistry Laboratory utilizing a Shimadzu RF5000U scanning spectrofluorophotometer, lab-developed methodologies and electronic data storage and processing (Fay, et al, this publication). Pure optical brighteners were obtained from Ciba-Geigy (1989) [Trademark: Tinopal CBS-X (ASTM DSBP-1) and Tinopal 5BM-GX (ASTM DASC-4)] to provide reference spectra for the two most common optical brightener derivative groups. Because of the proprietary nature of laundry product formulations, popular liquid and solid detergents were purchased, fluorometrically analyzed and compared with the pure optical brightener reference spectra. Excitation, emission and synchronous scans of calibrants, blanks and samples were conducted, and 60 nm synchronous scans were utilized to match 440 nm reference and sample peaks yielding positive FWA detections above the background cotton blank spectra. Several to many scans were run of each sample to ensure surface area coverage, and indeterminate results were treated as negatives.

***Water Supply Sampling and Analysis***

Sites were sampled periodically from taps supplying cold, untreated water close to the well. Water was allowed to run for 45 or more minutes until stabilized, i.e., 1 percent or less variation of temperature, pH, oxidation-reduction potential, specific conductance and dissolved oxygen. Stabilization instruments (YSI, Inc.: Model 3560 Water Quality Monitoring System and Model 50B Dissolved Oxygen Meter) were calibrated before each sampling event and then cleaned and rinsed with distilled water thereafter. Sample taps were flamed with a propane torch, and then water was allowed to run an additional 5 minutes before sampling. Appropriate sample containers, preservatives and coolers were utilized in accordance with Standard Methods (APHA, AWWA, WEF, 1992), as were the analytical protocols for the examination of the water samples whether in the field [e.g., total and bicarbonate alkalinity (titration) and ammonia/ammonium-nitrogen (Orion Model 290A ion selective electrode meter)], at contracted Minnesota Department of Health-certified environmental laboratories or the University of Minnesota Hydrogeochemistry Laboratory. A field and laboratory quality assurance plan was followed to ensure the representivity, precision and accuracy of the test results.

## RESULTS AND DISCUSSION

Thirty-five sites were selected among the four communities with the majority sampled periodically over the 1993-1995 project period. Table 2 summarizes fluorometric, physicochemical and bacteriological data collected with mean, range or percent positive reported for selected analytes.

**Table 2. Water Supply Test Data and Optical Brightener Detections from Four Communities**

| Parameter | Castle Rock | Coates | Empire City | Vasa |
|---|---|---|---|---|
| Sample Sites | 7 | 9 | 4 | 4 |
| Positive FWA's | 29% | 89% | 50% | 75% |
| pH (units) | 7.06 [6.75 ~ 7.33] | 7.13 [6.48 ~ 7.65] | 7.15 [6.66 ~ 7.42] | 7.05 [6.33 ~ 7.32] |
| Redox Potential (mV) | +146 [-56 ~ +212] | +146 [+123 ~ +166] | +140 [+111 ~ +173] | +132 [+117 ~ +149] |
| Conductivity (mS/m) | 82.8 [71.3 ~ 108.3] | 83.3 [59.8 ~ 120.1] | 60.9 [41.1 ~ 69.7] | 84.3 [69.0 ~ 119.8] |
| Tot Dis Solids (mg/L) | 509 [446 ~ 650] | 513 [383 ~ 715] | 389 [280 ~ 437] | 518 [433 ~ 713] |
| T Hard (mg CaCO3/L) | 386 [346 ~ 475] | 388 [305 ~ 516] | 309 [240 ~ 340] | 391 [338 ~ 515] |
| Tot Coli Bacteria-pos | 22% | 18% | 14% | 25% |
| Nitrate-N (mg N/L) | 7.9 [<0.2 ~ 15.5] | 11.8 [6.8 ~ 20.4] | 8.5 [0.2 ~ 12.2] | 8.2 [0.6 ~ 13.0] |
| Chloride (mg/L) | 64 [26.7 ~ 131] | 67 [14.2 ~ 110] | 18.6 [15.8 ~ 26.6] | 65 [36 ~ 111] |
| Sulfate (mg/L) | 45 [24.7 ~ 62] | 30.5 [28.0 ~ 33.1] | 24.2 [22.7 ~ 25.6] | 37 [24.0 ~ 55] |
| Tot Alk(mg CaCO3/L) | 259 [221 ~ 340] | 262 [205 ~ 355] | 220 [195 ~ 255] | 260 [225 ~ 375] |

*NB: One or more samples/site; mean [minimum~maximum]; percent positive; T / Tot = total; mV = millivolts; mS/m = millisiemens/meter = 10 umhos/cm; mV = millivolts; mg/L = milligrams/liter; N = nitrogen; CaCO3 = calcium carbonate*

Immersion filter holder media, depending upon length of exposure, water quality and other factors, were prone to physical erosion (surficial cotton fibers), masking by precipitates (e.g., carbonate scaling, iron hydroxides and staple corrosion), bacterial colonization (e.g., iron bacteria) and adsorption site competition. At spring sites, the physical removal of cotton fibers was aided and abetted by colonized bacteria and their consumption by grazing aquatic invertebrates. Despite cotton's sorptive affinity for optical brighteners, negative or indeterminate fluorometric results were sometimes reported when one or more of the above conditions occurred.

*Castle Rock*

Castle Rock was selected because of available water quality data and continuing investigations of significant groundwater impacts from former herbicide spill and rinsate disposals (Minnesota Superfund Site), residential and commercial waste dumping and road salt stockpiling, as well as the presence of nonconforming and failed septic systems (cesspools, seepage pits and nonconforming drainfields). Originally, 18 sites were chosen, but a County-sponsored well replacement project during 1993-94 removed 11 sites from this study. Before 10 of the 11 existing wells were disconnected and sealed, abbreviated screening tests were conducted with negative results for optical brighteners.

However, one well (site 1009) disconnection was delayed several months allowing additional exposure time and strong positive optical brightener results (Figure 2). These results are compared with site 1033 which has been consistently negative. Because the owner of site 1009 had plumbed the toilet with hot water to prevent condensation during the summer months, we surmise that cotton sorption of optical brighteners was enhanced by increased water temperatures. Optimum FWA adsorption varies with its solubility in water, temperatures between 15 and 50 degrees Celsius and other factors (Ciba-Geigy, 1989). Since ambient groundwater temperatures are colder (7 to 12 degrees Celsius), the obvious answer was to prolong the filter holder exposure time. Unfortunately, increasing the period of immersion to facilitate slower FWA adsorption likewise increases the masking of the cotton by precipitates and bacterial colonization which reduces the available surface area for FWA adsorption.

Completing the sampling and analysis of the remaining sites may provide additional clues to FWA detection problems in moderate ionic strength groundwater environments with mixed-source contaminants.

*Coates*

The City of Coates was chosen for its thick unsaturated zone of outwash sand and gravel overlying weathered dolostone, its proximity to large agricultural tracts and the Rosemount Research Center (National and Minnesota Superfund Site), and the prevalence of nonconforming septic systems (cesspools, seepage pits and deep, undersized drainfields). Rapid recharge and oxidation accounts for the consistently elevated nitrate, total dissolved solids, chloride and some fecal bacteria breakthrough (Table 2.). These correlated well with the 89% positive optical brightener detection rate although earlier samples at the same sites were less likely to be positive. As with Castle Rock, the early Coates negative results probably represent the early stage of the study when methods and materials were being refined, as well as possible dilution of optical brighteners during heavier precipitation periods.

Figure 3 compares an early low positive optical brightener detection from site 1034 [positive coliform bacteria and elevated nitrate (7.6 mg N/L)] with indeterminate results from site 1031 [negative coliform but very high nitrate (20.0 mg N/L)]. Subsequent sampling has given consistent positive results for site 1034 along with repeated positive coliform bacteria. There has been a single positive FWA result for site 1031 but continuing negative results for site 1030 which is adjacent and cross-gradient to site 1031, has a shallower well but similar nitrate, TDS, chloride and other water test results.

Figure 2. Fluorometric Scans - Castle Rock

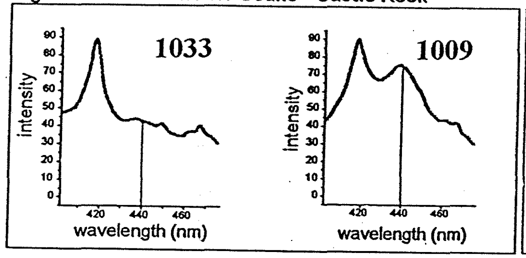
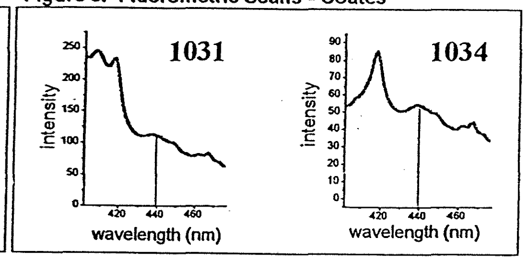



Figure 3. Fluorometric Scans - Coates




*Empire City*

Situated in an alluviated and outwash-filled buried bedrock valley and on and adjacent to the floodplain of the Vermillion River, the village of Empire City is characterized by a very shallow water table in highly permeable sand which has invited drivepoint well installations in basements in close proximity to septic systems (older, nonconforming drainfields and seepage pits are common) and other waste disposal.

Figure 4 contrasts a downgradient well location (site 1035) having a positive detection for optical brighteners on cotton at 440 nm with an upgradient well (site 1028) which yielded indeterminate results. The downgradient well water persists with positive FWA detects but slightly lower nitrate values (9.6-11.0 mg N/L) while the upgradient well is now positive for optical brighteners with nitrate at 11.8 to 12.2 mg N/L. All coliform bacteria tests have been negative.

However, in contrast, a reportedly shallower drivepoint at site 1038 located even farther downgradient than site 1035 has been consistently negative for optical brighteners and coliform bacteria. Nitrate has been 0.2 mg N/L, but most of the other parameters are similar to the water quality of the more upgradient wellpoints. The site is within the floodplain and that may hold the answer to the differences cited.

*Vasa*

An unincorporated village in Goodhue County, Vasa occupies a loess and till-capped upland ridge underlain by weathered sandstone and dolostone, both of which crop out in the vicinity. It appears that locally the fractured and karsted dolostone provides sufficient groundwater for the shallow wells completed in it but is also prone to pollution from waste and wastewater disposal practices. Several residents still utilize both rainwater and groundwater cisterns, but their proximity to deep, nonconforming septic systems and possible interconnection with well-supplied household water are problematic. It appears that all of the older, functioning wells are completed in bedrock with some of the shallower dug wells, now dry, having been converted to sewage pits.

As with the above examples, Figure 5 compares site 4040, formerly with indeterminate optical brightener results, to site 1041 located to its east and slightly downgradient which has had consistently positive detections. Both sites are routinely positive for FWA's now. Another positive FWA site (1045) is northwest and situated slightly downgradient from site 1040. Originally a shallower well, it was "deepened" a number of years ago to a reported 250 feet. However, its water quality is similar to that of the shallower bedrock wells.

Figure 4. Fluorometric Scans - Empire City

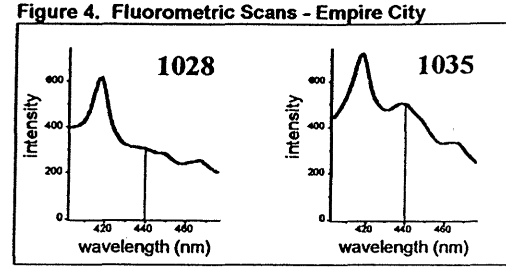
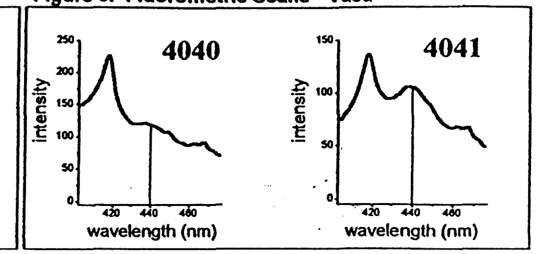



Figure 5. Fluorometric Scans - Vasa




## CONCLUSIONS

Employing novel methods for immersion and in-line sampling of cotton and other selective filter media and solid-phase, scanning spectrofluorophotometric techniques and computer-processed spectral analysis, the development of cost-effective qualitative screening and possible semi-quantitaive testing of optical brighteners (fluorescent whitening agents or FWA's) in groundwaters has been demonstrated in the field and laboratory. The methods obviate the concerns of fluorescent dissolved organic carbon compound interference that hampers low fluorometric detection limits for aqueous samples. Instead, they rely on solid media which preferentially sorbs and accumulates FWA's. By electronically storing excitation, emission and synchronous scans of sample spectra, comparing the results to optical brightener reference spectra at 440 nm, and resolving cotton or other filter media blank interference, relatively low detection limits are feasible. Preliminary correlations with sample site groundwater test data and sanitary survey information on water supply and waste/wastewater practices suggest moderately good agreement in utilizing positive optical brightener detections as indicators of septic system contamination of shallow, unconfined aquifers. The study will be completed with additional sampling and analysis to verify the optical brightener detection system and statistically correlate the data and information. The methods and materials are readily transferrable to surface water and wastewater optical brightener screening and testing.

## ACKNOWLEDGEMENTS

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ATTACHMENT 3.

# Optical Brighteners: Sorption Behavior, Detection, Septic System Tracer Applications

Steffan R. Fay[1], Ronald C. Spong[2], Scott C. Alexander[1], and E. Calvin Alexander, Jr[1].


## ABSTRACT

Laboratory soil column experiments were used to evaluate the optical brighteners (fluorescent whitening agents) Tinopal[3] CBS-X (ASTM designation DSBP-1) and Tinopal[3] 5BM-GX (ASTM designation DASC-4) and the fluorescent dye eosin Y (C.I. 45380) as adsorbing tracers in subsurface systems. In a low organic carbon content glacial outwash sand (foc = -0.0034, 97% sand by weight) the solid-water distribution coefficient (Kd) was determined to be 0.26 cm^3/g for Tinopal CBS-X, 0.78 cm^3/g for Tinopal 5BM-GX, and 0.024 cm^3/g for eosin Y. All three compounds had simple sigmoidal breakthrough curves.

Optical brighteners can be detected in direct solution by fluorometry but suffer from interference associated with naturally occurring organic compounds. Unbrightened cotton can be used to qualitatively detect optical brighteners. Polyethersulfone filter media can be used to selectively remove optical brighteners from solution without changing the background fluorescence spectrum. The exposed filter medium can be analyzed as a solid sample in a scanning spectrofluorophotometer. The resulting spectrum can be used to measure the optical brightener concentration in the filtered sample. Polyethersulfone filters can be used to detect optical brighteners in samples collected in and around septic system drain fields at less than 1 ppb Tinopal 5BM-GX equivalent.



## KEYWORDS

Optical brighteners, fluorescent whitening agents, detection systems, groundwater tracers, septic systems.


## INTRODUCTION

Fluorescent dyes are used extensively for tracing surface water and groundwater because of their low detection limits, ease and economy of detection, availability and safety. Fluorescent dyes have successfully been used to delineating otherwise unpredictable groundwater basins in karst environments (Quinlan and Ray, 1981; Alexander and others, 1993). Fluorescent dyes have also been used as adsorbing tracers in an effort to predict the breakthrough of pesticides in agricultural settings (Sabatini and Austin, 1991; Everts and Kanwar, 1994.)

Optical brighteners (also known as fluorescent whitening agents) absorb ultraviolet light and fluoresce in the blue region of the visible spectrum. The main commercial use of optical brighteners is in laundry detergents and textile finishing. Consequently, optical brighteners are relatively inexpensive and have been subjected to rigorous toxicity testing. Optical brighteners are found in domestic waste waters having a component of laundry effluent, and therefore can enter the subsurface environment as a result of ineffective sewage treatment. The potential exists to use optical brighteners as tracers of sewage effluent in polluted aquifers and as artificial tracers in pristine aquifers. In either case an understanding of the interaction between the dye and solid aquifer material is required to properly interpret tracer test results.

A great deal of information is available on the characteristics and behavior of the most frequently used dyes: rhodamine WT (RWT) and uranine C (URC) also known as fluorescein (Smart and Laidlaw, 1977; Everts and others, 1989; Shiau and others, 1993.)

This paper describes three aspects of our investigation into the potential use of optical brighteners as subsurface tracers. A soil column was used to compare the transport behavior of optical brighteners and the fluorescent dye eosin Y (EOS) to URC and RWT. We discuss a methodology for detecting optical brighteners on cotton using a scanning spectrofluorophotometer, and report the discovery and preliminary field results of a novel detection method utilizing polyethersulfone filter media.

Laboratory experiments were conducted with two stock optical brighteners supplied by the manufacturer. Both compounds are designed for use in domestic laundry detergent formulation at concentrations up to 0.5% on weight of formulation. Tinopal[3] CBS-X (TCBS) is a distyrylbiphenyl type whitener (see figure 1). TCBS is chlorine bleach stable in solution, has a high solubility (30% at 95C, 2.5% at 25C) and high fluorescence efficiency (Ciba, 1987). Tinopal 5BM-GX (T5BM) is a cyanuric chloride/diaminostilbene disulfonic acid derivative whitener (see figure 1). T5BM is beach stable only when sorbed to a substrate, is less soluble (1.5% at 50C) and has a lower fluorescence efficiency (Ciba, 1987). The optimal temperature range for sorption of both brighteners is in the 15C to 50C range.


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[3] Tinopal is a registered trademark of Ciba-Geigy Corporation, Greensboro, North Carolina, USA.

## SORPTION BEHAVIOR

Laboratory soil column experiments were conducted using a 30 cm (11.8 inch) long, 2.5 cm (1.0 inch) diameter borosilicate glass chromatography tube. Column end fittings and tubing were PTFE, with the exception of a silicone peristaltic pump drive section. The column was filled with repacked Rosemount Outwash aquifer material, obtained from a sand quarry near Coates, Minnesota. Column running parameters are listed in table 1. Organic carbon content was determined at the University of Minnesota Soil Science Research Analytical Laboratory. Column material grain size distribution was measured by standard sieve methods. Fines fraction was determined by inspection under an optical microscope. Hydraulic conductivity was calculated with the Hazen equation (see Freeze and Cherry, 1979, p. 350).

Table 1. Soil Column Parameters

| | | | |
|---|---|---|---|
| Column internal volume (cm^3) | 150 | Hydraulic conductivity by Hazen method (cm/s) | 1.4E-02 |
| Fraction organic carbon content, foc | 0.0034 | Porosity, n | 0.30 |
| Median grain size diameter, d50 (mm) | 0.34 | Repacked bulk dry density, ρb (g/cm^3) | 1.85 |
| Uniformity coefficient, d60/d10 | 2.8 | Pore water velocity (cm/h) | 30 |
| Sand: coarse, medium, fine (%) | 3, 37, 57 | Hydrodynamic dispersion coefficient, Dx (cm^2/h) | 3.4 |
| Fines: silt, clay (%) | 3, <1 | | |

Breakthrough data were collected in three separate column runs. The column was not repacked between runs. The breakthrough of a 1.0 g/L solution of sodium chloride (run #1) was used to calculate column parameters. Hydrodynamic dispersion coefficient, Dx was extracted from an analytical solution to the advection dispersion equation for saturated porous media (see Freeze and Cherry, 1979, p. 391) fitted to the chloride breakthrough curve. Chloride concentrations were determined by mercuric nitrate titration of column discharge aliquots. Approximately five pore volumes of water with no NaCl added were used to flush the column following run #1. Run #2 involved a 20+ pore volume continuous input of a mixture of URC, RWT and TCBS. Run #2 was followed by approximately 50 pore volumes of flushing. Run #3 was conducted using a continuous input of EOS and T5BM. Column runs were conducted in darkness or under subdued red lighting to minimize potential dye photodegradation, at approximately 25C.

Background ion concentrations have an effect on the transport characteristics of fluorescent dyes (Sabatini and Austin, 1991; Everts and Kanwar, 1994), so a pristine groundwater solvent was used in place of the traditional deionized water in an effort to more closely simulate field conditions. Groundwater was obtained from a flowing artesian well completed in the southern Minnesota Mount Simon aquifer. The water has previously been carbon-14 dated at over 10,000 years and contains no anthropogenic contaminants.

The fluorescent spectrum of the column discharge was monitored in the flow-through cell of a Shimadzu RF5000U scanning spectrofluorophotometer. Essential settings are listed in table 2. A synchronous scan mode was used at the detection wavelength separations (Δλ) listed. The relative dye concentration (C/Co) was determined from the area of characteristic peaks in the discharge fluorescence spectrum, e.g. C/Co(TCBS) = area of 440 nm peak in discharge / area of 440 nm peak in influent dye mixture (see figure 2.)

Table 2. Dye Properties

| Dye (ASTM designation / color index) | TCBS (DSBP-1) | T5BM (DASC-4) | URC (C.I. 45350) | RWT (Acid Red 388) | EOS (C.I. 45380) |
|---|---|---|---|---|---|
| Source | Ciba-Geigy | Ciba-Geigy | Fisher | Crompton Knowles | Fisher |
| Grade | commercial | commercial | purified | 20% solution | 88% powder |
| Batch # | 34918038 | 1009 | A-833 | 38 | 916991 |
| Concentration, Co (ppb) | 370 | 360 | 150 | 230 | 450 |
| Detection Δλ (nm) | 95 | 95 | 15 | 15 | 15 |
| Peak emission λ (nm) | 440 | 440 | 508 | 573 | 525 |
| Retardation factor, Rf | 2.6 | 5.8 | 1.04 | – | 1.15 |
| Kd (cm^3/g) | 0.26 | 0.78 | 0.006 | – | 0.024 |
| Koc (cm^3/g) | 76.5 | 229 | 1.76 | – | 7.06 |

Note: Peak emission wavelength and detection wavelength separation refer to analysis of direct solution samples.

Peak areas were calculated by integration of a best fit non-linear function. Figure 2 illustrates the Co concentration fluorescent spectra of all the dyes except T5BM, which has a shape identical to TCBS. Each symbol in figure 2 is a discrete data value in the fluorometer scan output. The black lines in figure 2 are the fitted curves from which areas were calculated, they do not just link the symbols. The peaks of URC, EOS and RWT were adequately described by a single peak function, with a linear or no background function. TCBS and T5BM were each described by a complex function made up of three simple peaks functions (not shown) superimposed on a small background peak (not shown). The subtraction of a background peak was required in the analysis for the optical brighteners to remove the effect of naturally occurring organic compounds which fluoresce in a similar region of the spectrum.

Retardation factors (Rf) were calculated as the number of pore volumes required to reach half influent concentration ($C = Co/2$). The solid-water distribution coefficient (Kd) was backed out of the expression $Rf = 1 + (\rho b / n) \cdot Kd$, where n = porosity and $\rho b$ = bulk density. The organic carbon-water distribution coefficient (Koc) was calculated from the expression $Koc = Kd / foc$, where foc = fraction organic carbon in the aquifer material.

**Figure 1. Chemical Structures of Dyes**

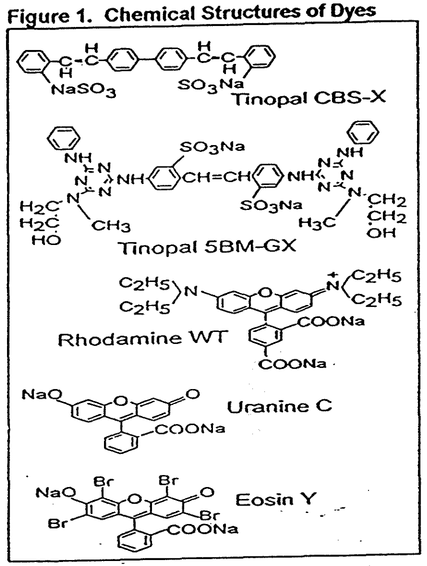
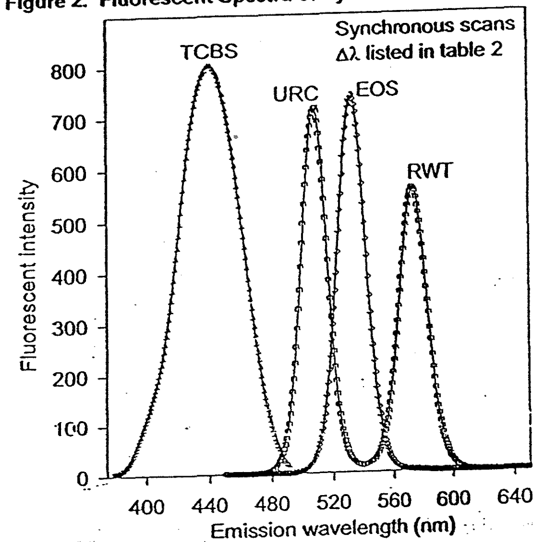



**Figure 2. Fluorescent Spectra of Dyes**




Results

Figure 3 summarizes the column experiment results. Each symbol in figure 3 represents a discrete data point derived from a single fluorometer scan. Chloride breakthrough exhibited the normal sigmoidal shape characteristic of saturated flow in a relatively homogenous porous medium, reaching $C = Co/2$ at 1.0 pore volumes. URC and EOS where the earliest dyes to breakthrough, both reaching $C = Co/2$ within 1.2 pore volumes. Optical brighteners were significantly retarded. RWT showed the characteristic stepped breakthrough attributed by Sabatini and Austin (1991) and Shiau and others (1993) to differing transport properties of two RWT structural isomers.

Retardation factors and distribution coefficients are listed in table 2. The complex breakthrough curve of RWT precludes the calculation of a single, meaningful value for its Rf, Kd and Koc. An additional column experiment using a 1.0 pore volume input followed by flushing showed that sorption of TCBS to aquifer material is reversible. Over 94% of input dye mass was recovered within 15 pore volumes of flushing (results not shown).

The Kd values obtained for URC from this experiment are approximately 1 order of magnitude lower than the results of Sabatini and Austin, 1991 (Kd = 0.05 cm^3/g) who used a very similar apparatus, porous medium and method. The source of this discrepancy is being investigated.

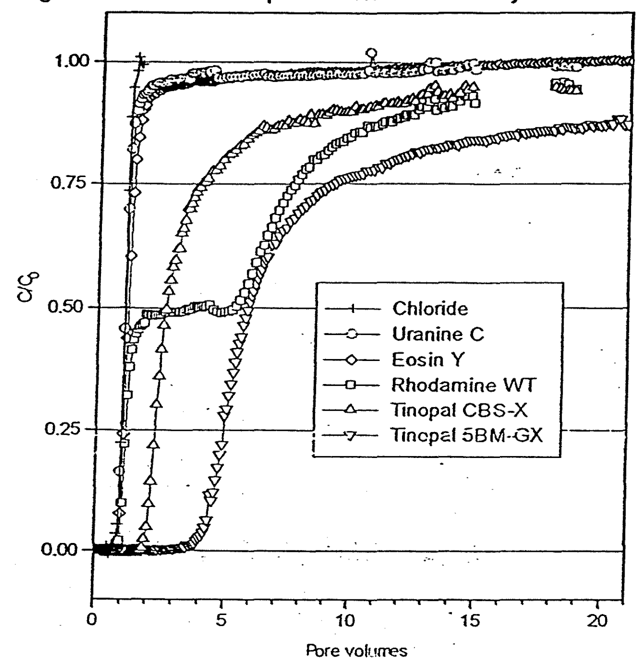
Conclusions

The breakthrough curve for EOS in this experiment was almost identical to that of URC. The symmetrical substitution of four Br atoms for four H atoms on the URC structure (see figure 1) does not appear to significantly affect the molecule's adsorption properties. EOS appears to be a good alternative to URC for tracer applications where retention on aquifer material is undesirable. EOS has the benefit of having a peak fluorescence emission wavelength higher than that of URC (see table 2 and figure 2). This characteristic reduces the potential for interference with naturally occurring fluorescent compound which tend to be concentrated at shorter green and blue wavelengths.

As stated by earlier authors, interpretation of RWT tracer test results requires an appreciation for its complex breakthrough pattern. In the absence of other tracer data the double stepped breakthrough of RWT could be misinterpreted as being indicative of multiple dye pathways.

TCBS and T5BM are potentially useful tracers. Although the detection of both dyes is subject to interference from other compounds, analytical developments can remedy that problem. A promising analytical improvement is discussed later in this paper. TCBS and T5BM are not distinguishable fluorometrically, ruling out their concurrent use. However, their simple sigmoidal breakthrough curve and differing retardation factors means that they could be used for predicting the breakthrough of various retarded contaminants, with perhaps less ambiguity than RWT. The strong sorption characteristics of optical brighteners improves their utility as indicators of failing septic systems where the soil adsorption property may have broken down.

**Figure 3. Soil Column Experiment Results Summary**




COTTON DETECTION SYSTEM

While optical brighteners are readily detectable by fluorometry at the part per billion level in laboratory prepared solutions, problems exist with extending this method of analysis to field samples. A primary cause for concern is the presence of variable concentrations of naturally occurring organic compounds which fluoresce at similar wavelengths to optical brighteners in solution. Figure 4 is a synchronous fluorometer scan ($\Delta\lambda$ = 95 nm) which shows the spectra of both a pristine groundwater and a dilute solution of T5BM. These complications lead Alhajjar and others (1990) to conclude that optical brighteners are not suitable indicators of septic system impact on groundwater. These authors' limitation of their optical brightener data to filter fluorometer analyses on direct water samples demonstrated the ineffectiveness of wide-band groundwater fluorescence. Their work does not, as they assert, indicate that optical brighteners can not be used as tracers of septic system effluent.

Aley (1985) successfully used a detection system based on unbrightened cotton to identify sewage impacts on karst groundwater. Quinlan (1981) used optical brighteners as artificial tracers employing a similar cotton based detection system. The use of cotton detectors exploits the strong sorption affinity of optical brighteners for cotton. We are currently using a spectrofluorophotometer to analyze cotton detectors as part of a regional survey of septic system impact on domestic wells in southern Minnesota described by Spong and others (1995, this publication.)

The application of a dilute solution of T5BM to unbrightened cotton produces a characteristic peak in the fluorescence spectrum of the material at approximately 440 nm. Figure 5 is a synchronous fluorometer scan ($\Delta\lambda$ = 60 nm) which shows the spectra of unbrightened cotton and cotton doped with a dilute solution of T5BM. Note that the sharp peak at approximately 415 nm is present in both signals. TCBS and powder and liquid formulation domestic laundry detergents produced identical results (not shown). The cotton detection system is based on the recognition of the characteristic peak in the cotton spectrum at 440 nm after exposure of the cotton to waters containing optical brighteners. A sample is considered positive for optical brighteners when the characteristic peak is present.

Figure 4. T5BM Detection in Direct Solution

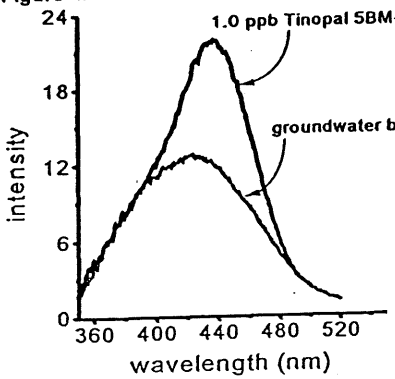
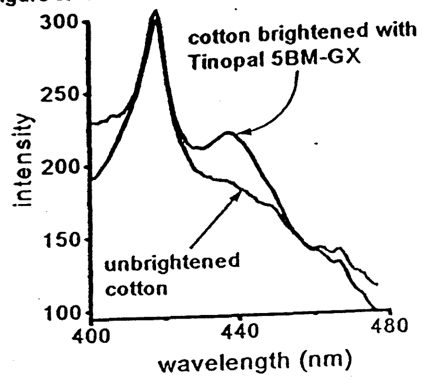



Figure 5. T5BM Detection on Cotton

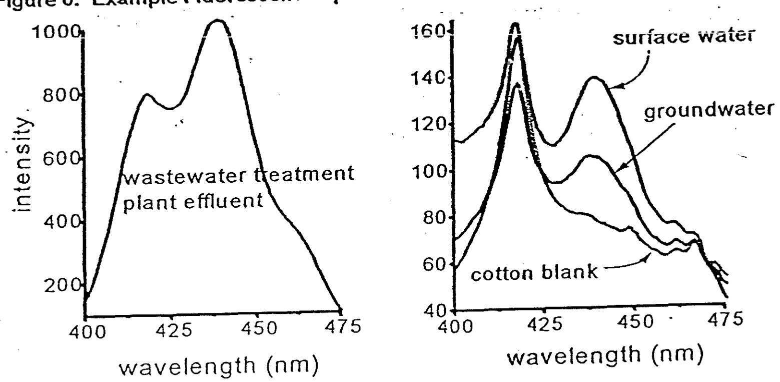



Results

Optical brighteners have been detected in a variety of water environments. Spong and others (1995, this publication) summarize the results of a regional survey of optical brighteners in shallow water table aquifers. Figure 6 contains some typical positive sample scans. All of the spectra in figure 6 are synchronous scans ($\Delta\lambda$ = 60 nm) of cotton samples. Note that the graph on the left side of figure 6 (cotton after exposure to the effluent stream of a waste water treatment plant) has a much larger y axis, indicating a greater degree of brightening.

Long term exposure of the cotton to a supply of the sample water (of the order of weeks) is typically required (see Spong and others, 1995). While increasing exposure time improves the chance of detection by allowing more of the sample water supply to encounter the cotton detector problems arise with bacterial colonization, mineral precipitation and cotton fiber loss. These phenomena tend to lead to heterogeneous brightening of the cotton surface, requiring multiple scans of various parts of each sample and restricting the cotton detection method to a qualitative positive/negative determination.

Figure 6. Example Fluorescence Spectra of Cotton Samples Positive for Optical Brighteners




NOVEL POLYETHERSULFONE DETECTION SYSTEM

This section of the paper describes our investigation into an improved detection methodology for optical brighteners. Syringe tip filter capsules are frequently used to remove suspended solids in the preparation of water samples for dissolved species analysis. One material used in the construction of such filters is polyethersulfone (PES). PES filters appear to selectively absorb optical brighteners.

The Acrodisc[4] (AD) and Acrodisc PF (ADPF) products both use PES as a filtration medium. Both products are housed in a 25 mm diameter modified acrylic housing, having an effective filtration area of 2.8 cm^2 (Gelman, 1994). The AD model that we tested has a 0.45 µm PES filter. We also used the ADPF which utilizes a 0.2 µm PES filter preceded by a 0.8 µm PES prefilter. Our investigation of the AD and ADPF filters consisted of three separate series of experiments:

***Experiment #1 (Dye scavenging efficiency of PES):*** Dye solution mixtures used for earlier column experiments (see table 2) were used to test the degree to which PES filters remove fluorescent dyes and optical brighteners from solution. In each experiment 3 ml of dye mixture solution was forced through an AD filter with a single-use 3 ml syringe directly into a 3 ml acrylic fluorometer cuvette. A 1 ml air purge was used, in accordance with the filter manufacturer's instructions, to remove liquid held on the filter by surface tension. The solution which had passed through the PES filter was analyzed and compared with an unfiltered (U) dye sample. The method of dye solution analysis was identical to that described in the "sorption behavior" section, above. To investigate the effect of filtration through an inert medium a 1.0 µm pore size glass fiber (GF) filter was also evaluated. Each dye/filter combination was tested in triplicate.

***Experiment #2 (Relationship between sorbed mass and fluorescence):*** The solid sample holder of the fluorometer allows the analysis of materials such as the PES filter medium. In a series of experiments a known mass of dye was applied to individual ADPFs using the syringe method described above, with the addition of a 9 ml deionized water rinse. After exposure the filter casing was broken open, and the filter medium removed. The fluorescent emission spectrum of the filter medium was measured between 380 nm and 525 nm, holding an excitation wavelength of 370 nm. Five samples were examined for photodegradation during analysis. After an initial scan samples were allowed to remain in the path of the fluorometer excitation beam (set at 650 nm) for approximately 2 minutes, and then reanalyzed. This time frame brackets the normal period which would be allowed to lapse between placing the sample in the fluorometer and initiating the emission scan.

***Experiment #3 (Effect of natural background organic compounds):*** A sample of lake water containing no optical brighteners, but relatively rich in natural organic compounds was filtered through ADPF. This experiment was conducted to measure the degree to which naturally occurring organic compounds might adhere to the PES medium and interfere with optical brightener detection.

Results

Figure 7 graphically displays the results of experiment 1. The x axis reflects the three treatments given the dye mixtures: unfiltered (U), glass fiber filtered (GF) or polyethersulfone filtered (PES). The connecting lines are a visualization aid only and have no physical interpretation. Box height at each x axis interval indicates the variability encountered in triplicate analyses. Figure 7 shows that while over 80% of both optical brighteners passed through the GF filter no TCBS or T5BM was detectable after passing through the PES filter. URC and RWT concentrations were slightly reduced by PES filtration. EOS was reduced to approximately 40% of unfiltered concentration. The GF filtered URC samples had an apparent concentration of 105% relative to unfiltered samples. This is possibly due to the removal of iron colloids and/or microscopic calcite laths. These particles were observed in the unfiltered groundwater and may slightly obscure the fluorescence of unfiltered direct dye samples.

Figure 7. Sorption to Filter Media

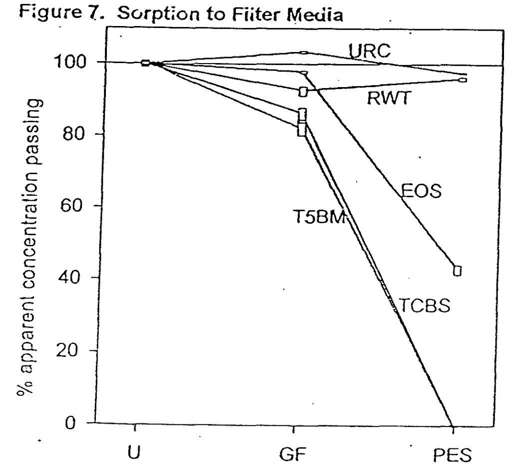



Figure 8. Tinopal 5BM-GX on Polyethersulfone

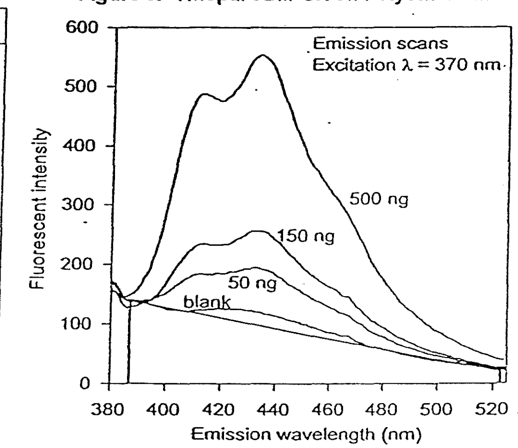



Figure 8 contains the fluorescence spectra of PES media with various masses of T5BM sorbed. A double peaked signal, which increases in area with increased sorbed dye mass, is evident. The main peak is at 434 nm with a secondary peak at 414 nm.

Figure 9 is a plot of emission scan peak area versus sorbed mass for TCBS and T5BM. Peak area was calculated by numerical integration of the fluorometric emission scan signal between 388 nm and 525 nm followed

[4] Acrodisc and Acrodisc PF are registered trademarks of Gelman Corporation, Ann Arbor, Michigan, USA.

by the subtraction of the underlying trapezoid (see fig. 8). The complex nature of solid phase fluorescence spectra precluded area integration with the non-linear curve fitting procedure described above for direct solution analysis. The linear best fit for T5BM is described by the function: mass (ng) = [peak area (fluorescent intensity . nm) - 667.9] / 55.18. The constant in this equation (667.9) represents the best estimate of the portion of the peak area attributed to unexposed "blank" PES.

In figure 9 vertical lines connect samples which were analyzed immediately and those which were allowed to remain the fluorometer excitation beam. Significant photodegradation is evident for T5BM, especially at higher concentrations. No degradation was observed for TCBS. The TCBS curve is steeper than the T5BM indicating more media brightening per mass of brightener sorbed. These observations are in accordance with the manufactures specifications.

Figure 10 summarizes the results of experiment #3. The lower box compares the emission scan spectra of the organic rich lake water before and after it was passed through the PES filter. The fluorescent signature is essentially unchanged which indicates no significant removal of fluorescent compounds by the filter. Note that the vertical scale of the lower part of figure 10 is much more expanded than that of figure 8 or the upper part of figure 10. The upper box compares the emission spectra of two PES filters, one exposed to the lake water and the other to deionized water. The lake water produced no significant enhancement on the PES filter compared to organic free deionized water. The same experiment comparing optical brightener free groundwater with deionized water produced identical results (not shown.)

Figure 9. Tinopal Calibration Curves

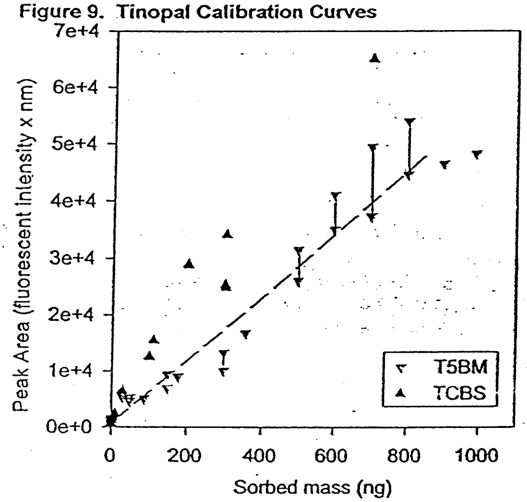
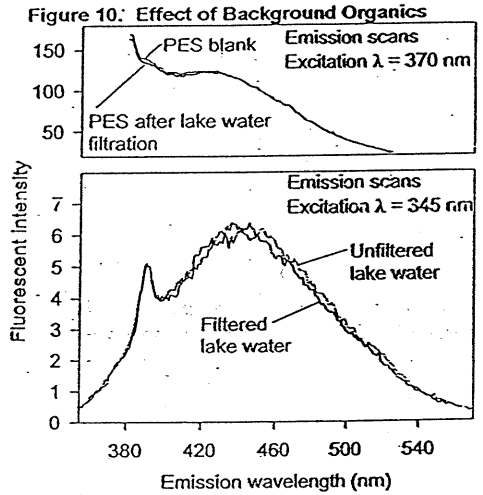



Figure 10. Effect of Background Organics




## Conclusions

PES filters quantitatively sorb optical brighteners from solution without simultaneously sorbing at least some naturally occurring organic compounds. We speculate that the mechanism responsible for the binding of optical brighteners to PES is related to the sulfonate functional groups present on both Tinopal compounds (see figure 1). T5BM is prone to photodegradation during fluorometric analysis when sorbed to the PES medium at higher concentrations. The phenomenon appears to be less important at lower concentrations.

Naturally occurring organic compounds in a lake water and groundwater sample did not interfere with optical brightener detection using PES filter media.

## SEPTIC SYSTEM TRACER APPLICATIONS

The detection methodology described above was used to analyze samples obtained from two instrumented septic systems located in rural southern Minnesota. The systems, identified here as A and B, were constructed in October, 1994 in heavy clay-till soils where shallow water table conditions generally prevail. Both systems are equipped with a curtain tile to locally depress the water table beneath the drain field. The system A drain field is situated in a topographically flat area. System B has a gravity fed drain field installed on a moderate slope. Both systems receive input from single family dwellings.

Water quality in and around the drain field is sampled through a series of lysimeters located at 30.5 cm, 61 cm and 91.5 cm (1, 2 and 3 feet) below the drain field pipes. Additional samples were obtained from the drain field influent. The optical brightener data discussed below come from a single sample set collected March 27, 1995. Other water quality parameters were recorded but are not discussed here.

For each sample between 36 ml and 72 ml of water were passed through and ADPF in the field. Filters were refrigerated in darkness until being broken apart and having the PES filter medium subjected to fluorometric analysis. Fluorometric spectra with discernible peaks in the region characteristic of optical brighteners were analyzed by the methodology described above. Peak areas were converted to an equivalent T5BM mass with the linear regression formula. Sorbed mass was converted to concentration based on known sample volume.

## Results

Peaks were visually noted to be very similar in shape to the T5BM emission signatures (fig. 8.) Optical brighteners were detected in five of the six lysimeter samples and one of the two septic system influent samples (see table 3.) The practical detection limit appears to be approximately 0.1 ppb T5BM equivalent, corresponding to the smallest discernible peak in the sample emission spectra of this sample set. The very brief presentation of this field data is used only to demonstrate that optical brighteners can be detected in field situations by the methodology outlined above. This technique is a component of ongoing research at these and other instrumented septic systems.

Table 3. Optical Brightener Concentrations (ppb T5BM equivalent)

| System | Influent | 30.5 cm | 61 cm | 91.5 cm |
|---|---|---|---|---|
| A | 8.4 | 0.3 | 1.6 | 3.2 |
| B | <0.1 | <0.1 | 0.8 | 0.1 |

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