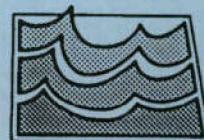

**REVIEW AND EXPERIMENTAL EVALUATION
OF EFFECTS OF SHORT-TERM PVC CONTACT
AND DISTILLED WATER WASH PROCEDURES
ON MEASURED PESTICIDE CONCENTRATIONS
IN FIELD SAMPLES**

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The effect of short-term contact with PVC (polyvinyl chloride) on the accuracy of measurements of organic contaminants in field water samples is of concern for many sample situations. Rigid PVC has been commonly used for the construction of sampling and monitoring wells. Rigid PVC is also one of the most common materials used in the construction of bailers. In many sampling situations, ground-water contact time with well casing during the process of purging and sampling is relatively short. Sample-water contact time with bailers during sampling is also short. The purpose of this report is to review existing literature concerning the effects of PVC contact on measured concentrations of organic contaminants in water; to experimentally examine the effects of short-term contact with PVC on measured concentrations of six commonly used agricultural chemicals in water; and to experimentally evaluate the efficacy of field distilled-water wash procedures in decontaminating PVC bailers during field sampling.

Summary and Review of Published Research

A review of the literature indicates that for sampling organic contaminants stainless steel is the least sorptive. The term "sorption" is used to describe the combined processes of adsorption and absorption. Rust and deterioration of stainless steel due to corrosive agents do not appear to increase the amount of sorption. All organic contact materials tested, including rigid and flexible polyvinyl chloride (PVC), polytetrafluoroethylene (PTFE), polyethylene, polyvinylidene fluoride, epoxy-impregnated fiberglass, and polypropylene were shown to cause sorption of organic contaminants. However, in most cases sorption was very slow, taking at least hours and usually days to reach significant quantities. Of these PVC was generally least sorptive. One author (Gillham and O'Hannesin 1990) ranked the materials in the order stainless steel > rigid PVC > fiberglass > polyvinylidene > PTFE > flexible polyethylene > flexible PVC in order of least sorption. Another (Miller 1986) reported that polyethylene and polypropylene were more sorptive than PVC. Flexible polyethylene and PVC are very sorptive, are capable of sorbing significant amounts of

analyte in a short period of time, and will frequently sorb nearly all of the analyte if given sufficient time to do so.

After 24 hours sorptive losses of up to 24 % have been indicated for PTFE. However, sorption of most contaminants on PVC was extremely slow, and in most cases did not exceed 10% after several weeks. Short term contact of organic contaminants with rigid PVC generally has no significant effect on sample analyte concentrations. However, there are some exceptions. One highly sorptive analyte is tetrachloroethylene, which appears to sorb more quickly (within several hours) than other compounds on PTFE and PVC. One problem of concern for PVC is lead, which given sufficient time, is very strongly adsorbed on PVC casing and may result in 50% or more loss from the sample solution.

Clues in identifying the tendency of a compound to sorb on a contact material include the octanol/water partition coefficient (K_{OW}), which has been found to be strongly related to the equilibrium coefficient for sorption of specific analytes on PTFE. There also appears to be evidence in the data of the literature that indicates that this applies to PVC as well. Generally, the larger the tendency to partition into octanol, the larger the rate and tendency of sorption on the contact material. The K_{OW} has been found to be least predictive for analytes having a strong tendency to hydrogen bond such as triazines, where sorption would tend to be overestimated.

Analytical interferences resulting from leaching of compounds from contact materials do not appear to be a problem of practical concern with rigid PVC (without plasticizers as in the more flexible laboratory tubing) or with PTFE. However, leaching of iron from steel casing can occur, so that PVC and PTFE are preferable for some trace metal analytes.

Summary of Bailer Contact Experiment

Our experimental evidence for pesticides bromoxynil (3,5-Dibromo-4-hydroxybenzonitrile), diclofop-methyl (methyl 2[4-(2,4-dichlorophenoxy)phenoxy]propanoate), dimethoate (o,o-dimethyl S-(N-methylcarbamoylmethyl)phosphorodithio

ate), MCPA (2-Methyl-4-chlorophenoxyacetic acid), methyl parathion (o,o-Dimethyl-o-[4-nitrophenyl] phosphorothioic acid), propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole), and trifluralin (2,6-Dinitro-N, N-dipropyl-4-trifluoromethylaniline), give no evidence that short term (about one minute) contact with a PVC bailer results in significant changes in measured analyte concentrations due to sorption.

Our data also indicated that the effectiveness of a distilled water (DW) wash alone in decontaminating pesticides from a PVC bailer was related to both water solubility and K_{OW} properties. Analytes having a water solubility of > 500 mg/L, or a K_{OW} value of < 200 were generally effectively cleaned from a PVC bailer so that no residual carryover in wash water was observed following a single thorough wash with DW. An exception was dimethoate. Analytes having a water solubility of > 50 mg/L or $K_{OW} < 2000$ were generally effectively cleaned from a PVC bailer following a multiple (>6 rinses) DW wash. Dimethoate was again an exception. With the addition of 15 bails with well water results were the same as for multiple DW washes, except that dimethoate was also effectively cleaned. For chemicals above threshold K_{OW} , or below threshold solubilities, exponential and power functions respectively described the relationship between cleaning effectiveness and K_{OW} and solubility properties.

General Conclusions

General conclusions of this review and experiment follow closely those of Parker et al. (1989), who indicated that stainless steel is best for organic contaminant sampling. However, of polymeric materials PVC is clearly the material of preference as a contact material for most organic contaminants under normal (low concentration) circumstances. sorption occurs, but sorption processes are slow, and for sample contact times of 24 hours or less none of the rigid materials tested (rigid polyethylene, polypropylene, PVC, fiberglass, polyvinyl fluoride and PTFE) should cause problems of significant concern for most organic contaminants. Flexible plastics, including polyethylene and PVC are highly sorptive and can cause almost total loss detection of some analytes.

Where data has been obtained following large contact times, sorption of more than 20% on any of the materials is rare, sorption of more than 10% for organic analytes on PVC over very long contact periods is exceptional. Interpretation can be assisted by remembering that generally analytes with larger K_{OW} , and lower water solubility have more tendency to sorb. As a caution, it should be remembered that sorption is always a function of the interaction of a specific analyte and the material itself, and exceptions can be found. Wherever possible, direct information on a specific contaminant of interest is desirable.

For detection levels used in this experiment the DW wash procedures alone should be reliable for removing residual contaminants where detected analyte concentrations are low, water solubilities of the analyte are high, and K_{OW} for the analyte is low. The lower the solubility, and the larger the K_{OW} for a given analyte, the greater the risk of cross contamination. For wash procedures in routine sampling, EPA field procedures (including low-phosphate soap wash, distilled water wash, solvent wash, and a final distilled water rinse to remove solvent leachate) should be followed. However, in some cases it may be justifiable and appropriate for cost and logistics reasons to rely on DW wash alone. Such sampling procedures should be based on known and demonstrated efficacy of the DW wash procedure for the specific target analytes in contact with a known and specific contact material, and in a known and appropriate detection range.

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INTRODUCTION

Health and economic concerns, and increased federal and state regulation of contaminants have brought about a need for reliable measurements of contaminants in ground water. Because of the extremely low levels at which some pesticides are considered unsuitable for human consumption, obtaining suitable samples and properly interpreting the results of those samples can be quite difficult. Some factors contributing to that difficulty are: (1) field sampling conditions such as wind, rain, dust, and floral and faunal influences which can cause sample contamination; (2) increasing accuracy of analytical procedures for detection of trace organic compounds, which frequently enable detections at levels where spurious contaminants from the field or laboratory might influence results; (3) ongoing uncertainties concerning appropriate well and sampling equipment, materials, and sampling procedures; and (4) historical practices which effect the quality of existing data and its interpretation.

The combined problems of refined laboratory detection levels and field sampling conditions can cause considerable difficulty in interpretation of field data. There is a point, although ill defined, at which errors due to field and laboratory procedures become difficult to separate (Spalding 1989). Information is required to determine optimal sampling methods and materials, but also to delineate the limits and weaknesses inherent in even the best of methods, and to assist in discerning the likelihood of spurious and misleading results encountered in the use of routine procedures.

The combined problems of historical practices and ongoing uncertainties also cause serious interpretive problems, and likely will continue to do so in the future despite attempts at standardization. Most state and federal agency sampling procedures for trace organics have evolved from sampling programs initially focused on inorganic water quality, and have required modification in response to problems encountered in the process of sampling. Of 30 states surveyed by Mickam et al. (1989), ten have no set policy or procedure for decontamination of equipment used for sampling trace organics, and negotiate procedures with contractors on a case by case basis.

Of the remaining 20 states, procedures vary from a recommended deionized water rinse alone (with recommended polytetrafluoroethylene [PTFE or teflon] or stainless steel contact material) for the state of Michigan, to variations of highly complex procedures requiring combined cleaning with low-phosphate soap, rinsing with assured contaminant free tap water, rinsing with deionized water, rinsing with single or multiple organic solvents, rerinse with distilled water, and drying. The United States Environmental Protection Agency (EPA), considered by many the primary standard setter for contaminant sampling procedures, has gone through a succession of procedural modifications. Although there are some national guidelines, EPA has historically had no single document governing sampling methods, and procedures have been routinely suggested by regional offices. Moreover, requirements frequently change because new data demonstrate that changes are necessary (Mickam et al. 1989). The November 1992 EPA RCRA Ground-Water Monitoring Draft Technical Guidance document does contain a review and recommendations for sampling procedures and well casing materials.

Attempts to standardize field procedures used for sampling trace organic contaminants are thus fraught with difficulties and dilemmas. While standardization is helpful, the field environment is extremely complex and variable. Contaminants themselves are also extremely complex, and their interactions with the field environment and with specific sampling materials and procedures are even more so. While guidelines are helpful and necessary, many situations will always require modification to meet local conditions. For example, handling of sampling equipment in the wind and dust of the great plains presents problems different from those of humid and forested areas, where precipitation might result in the introduction of trace volatile organic pesticides through rain water during sampling.

Conversely, cost is always an important factor, and elaborate decontamination procedures or specifications of expensive materials applied to chemical species that do not require those materials or procedures can be wasteful, and can cause disposal problems. It is not reasonable to require that specifications to assure the quality of detections for all analytes be applied to every individual analyte.

Specific analytical detection levels required must also be considered. A decontamination procedure that is suitable for cleaning sample equipment for detection of a pesticide in the part per billion range might not be adequate to prevent cross contamination in the part per trillion range. Conversely, it might be wasteful to apply overly elaborate procedures for detection levels that do not require those procedures. Finally, decontamination procedures themselves have associated problems, and may even cause further dilemmas in interpretation of data.

In addition to ongoing variations in sampling procedures and materials, there will always remain the fact that substantial data has been taken and gathered under conditions that may not be currently approved. Lacking other information, legislatures and regulatory personnel will have to use that information to the best of their ability in evaluating cases of ground water contamination and in assessing overall situations of ground water vulnerability and pesticide use impacts. For this reason, it is necessary that we not only work to develop appropriate procedures, but that we develop a progressively better feel for the effects of procedures that have been previously used, on detections of specific analytes.

The Polyvinyl Chloride Issue

A common procedure historically used for sampling inorganic water quality has been the purging of several (two to five) well volumes of water using a bailer. Rigid polyvinyl chloride (PVC) has been a common material for both well casing and bailers. The use of PVC has been challenged as a sample contact material because of possible sorption and subsequent leaching of contaminants and also because of possible deterioration of PVC by solvents. Common well construction also includes the use of solvent weld glues. The use of solvent weld glues has been discouraged because of contaminants leaching from the glues. Current EPA specifications recommend the use of threaded casing (USEPA 1992). Some use stainless steel screws to secure the joints of the casing.

Common bailer cleaning procedures for inorganic water quality samples have included well water rinse (or deionized water rinse) alone between samples. The use of

distilled or deionized water alone has also been indicated to be inadequate for proper decontamination of bailers used in sampling for organic contaminants.

Nonetheless, elaborate well monitoring networks using PVC casing and solvent welded casings exist in many states and may be needed for cost effective monitoring of pesticides. Moreover, substantial data from samples taken using deionized water or distilled water washes alone exist, and data from samples taken using PVC bailers also exist.

Despite all potential drawbacks, many wells used for monitoring and for sampling are placed near the ground water surface so that extensive bailing is not required. Also, most aquifers are highly transmissive so that recovery of wells during bailing is relatively rapid, and contact time between sample water and the well casing and the bailer is brief. Time of contact with well casing is typically not more than a few minutes. Time of contact for wells in low permeability formations, is often less than 24 hours. Contact time for bailers is typically about one minute.

The purpose of this experiment and report is to (1) examine the effect of a realistically brief contact time between a rigid PVC contact material (a bailer) and a sampled water volume on the measured concentrations of the pesticides bromoxynil (3,5-Dibromo-4-hydroxybenzoxynitrile), diclofop-methyl (methyl 2[4-(2,4-dichlorophenoxy)phenoxy]propanoate), dimethoate (o,o-dimethyl S-[N-methylcarbamoylmethyl]phosphorodithioate), MCPA (2-Methyl-4-chlorophenoxyacetic acid), methyl parathion (o,o-Dimethyl-o-[4-nitrophenyl] phosphorothioic acid), propiconazole (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole) and trifluralin (2,6-Dinitro-N, N-dipropyl-4-trifluoromethylaniline); (2) evaluate the effectiveness of bailer decontamination using distilled water alone for these analytes; and (3) evaluate the potential for cross contamination or spurious detection in a succeeding well following decontamination using distilled water alone.

PREVIOUS WORK

In recent years there has been considerable controversy concerning appropriate sample contact materials (such as well casing and bailers). One of the most common materials used for both well casing and sampling bailers is rigid PVC. A substantial portion of the monitoring well and sampling well network in place in the United States has been constructed with PVC. Moreover, a substantial data base collected with rigid PVC bailers has been established. In 1985, in the initial draft of EPA's RCRA Ground-Water Monitoring Technical Enforcement Guidance document (USEPA 1986), it was recommended that stainless steel, polytetrafluoroethylene (PTFE; commonly referred by the trade name Teflon), or another proven stable material be used for construction of sample wells. Concerns over corrosion of steel and deterioration of PVC, polyethylene, and polypropylene in contact with various organic species were cited. Moreover, the possibility of contaminant adsorption or leaching of contact material material constituents was cited.

However, Parker et al. (1989) pointed out that while degradation and corrosion of steel and polymeric substances was known to occur when exposed to high concentrations of neat solvents, the presence of such large concentrations was rare in ground water monitoring situations. From this they posited that "PVC casings may be suitable for monitoring organics in the concentration range most commonly found".

A realistic assessment of the effects of sample contact materials must consider many factors, including the adsorptive properties of the contact material; the physical and chemical attributes of specific contaminants, including water solubility, sorptive behavior, and the tendency of contaminants to form hydrogen bonds; rates of sorption; contact time of water sample with casing or bailer material; possible preconditioning effects based on the premise that contaminated ground water will have equilibrated with casing prior to sampling; differences in rates of adsorption and desorption; the nature of the sorptive process, which can cause differences (or similarities) in sorption at different contaminant concentration ranges; stability of the contact material in the presence of contaminants or desired analyte species, which can influence the possibility of false detections, analytical

blockages, or increased random noise (and commensurate standard errors) in analytical procedures; possible effects of cleaning and decontamination procedures, such as use of solvents, on contact material integrity; and the possible effects of accompanying structural materials such as glues and cements or material conditioners on material integrity. Although research on each of these facets is still far from complete, there is sufficient work to begin to draw some practical conclusions on the probable limitations inherent in the selection and use of contact materials. Much of the following literature review is a recapitulation and further discussion of materials previously discussed in an excellent review by Parker et al. (1989).

Adsorption

Several experiments on the adsorption of organic contaminants on various sample contact materials have been conducted. Miller (1982) tested polyethylene, polypropylene, and rigid PVC sample contact materials for adsorption and leaching of chromium (IV), lead, and volatile organics including bromoform [4 µg/L], tetrachloroethylene [2 µg/L], trichloroethylene [3 µg/L], trichlorofluoromethane [2 µg/L], 1,1,1-trichloroethane [2 µg/L], and 1,1,2-trichloroethane [14 µg/L]. Adsorption was measured weekly for six weeks. Total adsorption of tetrachloroethylene on PVC was approximately 50% after six weeks. No adsorption was indicated for the other five analytes for six weeks of material contact. Polypropylene and polyethylene well casing adsorbed significant amounts (varying from 25% to 100%) of all contaminants. As with PVC greatest adsorption (100% for both materials) occurred with tetrachloroethylene.

Armstrong (1989) reported, however, that samples of volatile organics (including benzene [0.5 to 550 mg/L], 1,2-dichloroethane [19 to 35 mg/L], ethylbenzene [3 to 700 mg/L], isopropylbenzene [7 to 15 mg/L], methylene chloride [15 mg/L], naphthalene [1 to 10 mg/L], n-propylbenzene [1 to 35 mg/L], toluene [1 to 2 mg/L], and 1,3,5-trimethylbenzene [10 to 19 mg/L] taken from contaminated wells using disposable polyethylene bailers did not differ from those taken using PTFE bailers. Armstrong's data seemed to indicate that there were more detects with the polyethylene bailer than with the

PTFE bailer. For inorganic contaminants, Miller (1982) observed that lead was highly (> 75%) adsorbed on PVC after six weeks. No loss of chromium (IV) was observed.

Reynolds and Gillham (1986) conducted tests of both PVC and PTFE contact materials for low levels (20 to 45 µg/L) of 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, bromoform, tetrachloroethylene, and hexachloroethane for periods of up to 5 weeks. They reported that their results were similar to those of Miller (1982), except that they observed 43% loss of bromoform with PVC after 5 weeks, while Miller observed no loss.

Gillham and O'Hannesin (1990) studied the adsorption of benzene, toluene, ethylbenzene, m-xylene, o-xylene, and p-xylene from dilute solutions (1 to 1.3 mg/L) over a period of several weeks on PTFE, rigid PVC, flexible PVC, flexible polyethylene, stainless steel, polyvinylidene fluoride, and an epoxy-impregnated fiberglass material. They found that the order of suitability was stainless steel > rigid PVC > fiberglass > polyvinylidene > PTFE > flexible polyethylene > flexible PVC. The stainless steel exhibited no adsorption for any of the analytes. The flexible PVC and polyethylene exhibited significant absorption of all analytes almost immediately, and eventually adsorbed almost all of the analyte. All others effected a slow adsorption of analyte.

Sykes et al. (1986) reported that after exposure to PVC, PTFE, and stainless steel contact materials for one hour and 24 hours, all measurements of selected volatile organic compounds (methylene chloride [133 µg/L], 1,2-dichloroethane [126 µg/L], trans-1,2-dichloroethane [128 µg/L], trichloroethylene [147 µg/L], toluene [87 µg/L], and chlorobenzene [110 µg/L]) were within one standard error of the mean of measured control samples. They concluded that there was no statistical difference between effects of PVC, PTFE, and stainless steel contact materials on measured results. While statistical significance was reported, the actual variance was not reported so that magnitude of error used in statistical analysis could not be assessed.

Gossett and Hegg (1987) tested recovery of chloroform [749 mg/L], benzene [439 mg/L] and 1,2-dichloroethane [628 mg/L] for PTFE and PVC bailers and found no significant difference in concentrations. Barcelona and Helfrich (1986) reported that 1,1-dichloroethane values were higher in stainless steel and PTFE wells than in a well with PVC

casing. Levels of cis-1,2-dichloroethylene were higher in stainless steel wells than in wells constructed of PTFE or PVC casing.

Parker et al. (1989, 1990) investigated adsorption of ten contaminants on PVC, PTFE, and stainless steel. Contaminants included RDX [1,3,5-trinitro-1,3,5-triazine, 1.79 mg/L], TNB [1,3,5-trinitrobenzene, 2.37 mg/L], CDCE [cis-1,2-dichloroethylene, 2.79 mg/L], TDCE [trans-1,2-dichloroethylene, 2.71 mg/L], MNT [m-nitrotoluene, 2.32 mg/L], TCE [trichloroethylene, 2.80 mg/L], CLB [chlorobenzene, 2.18 mg/L], ODCB [o-dichlorobenzene, 2.31 mg/L], PDCB [p-dichlorobenzene, 1.97 mg/L], and MDCB [m-dichlorobenzene, 2.27 mg/L]. Throughout the study PTFE was shown to have the greatest adsorption for all of the contaminants where losses were observed. After 1000 hours only RDX and TNB had no significant contaminant losses due to adsorption on PTFE. Losses of other contaminants ranged from as little as 10% for MNT to as much as 76% for PDCB and MDCB.

While significant adsorption for rigid PVC was indicated for five of 10 contaminants (TCE, CLB, ODCB, PDCB and MDCB) after 1000 hours, the maximum loss was 17%. Stainless steel was indicated to have no significant loss due to adsorption after 1000 hours. Parker et al. (1989, 1990) concluded that "PTFE was clearly the poorest choice of the four well casing materials tested when samples are to be analyzed for trace level organics. Significant losses of all the chlorinated compounds occurred within 1-8 hours, and one nitroaromatic compound was also lost after prolonged exposure (1000 hours)."

Recovery rates of approximately 80 to 100% were reported by Curran and Tomson (1983) for dichlorobenzene and naphthalene at 0.5 and 0.5 $\mu\text{g/L}$ after one pass through 1.25 cm-diameter 0.31 m-long columns made of PTFE, rigid PVC (glued and unglued), polyethylene, and polypropylene at approximately 30 ml/min. However, for Tygon recovery was less than 50%. While PVC recovery was slightly lower than PTFE recovery, losses were very small and variable. The authors speculated that lower loss rates compared with those previously reported were likely due to plasticizers in flexible PVC in previous experiments. Overall results are consistent with the results of Parker et al. (1989) and Miller (1982). Also Gossett and Hegg (1987) found no significant changes in

measurements of organic compounds from use of a PTFE or PVC bailer, or due to use of stainless steel or PTFE wells. Conversely, Miller (1991) reported that detections of the phenoxy herbicides MCPA, diclofop-m, and bromoxynil were consistently lower in PVC wells than in stainless steel wells.

Two problems should be considered in evaluating the above experimental evidence. First, for long-term contact experiments it is important that degradation of chemicals be accounted for. Only two of the above cited experiments (Gillham and O'Hannesin 1990 and Parker et al. 1990) included measures to suppress biological activity. Thus, in other studies loss due to biodegradation may be included with apparent reported adsorption data. In addition, field studies are subject to large spatial variability. Without very large sample populations there is considerable risk of interpretive error. These considerations should be kept in mind for the experiments of Barcelona and Helfrich (1986) and Miller (1991).

Time and Rate of Sorption

Although both PVC and PTFE were demonstrated to adsorb contaminants, and although PVC generally seem to adsorb less than PTFE after lengthy periods of contact, rates of sorption are an important consideration in evaluation of appropriate sample contact materials. Most of the data of Miller (1982) appeared to follow an approximately logarithmic decline in solution concentration. Tetrachloroethylene, which was about 50% sorbed on PVC after 5 weeks, was only 17% sorbed after one week. Thus, contact time appears to be a major consideration in evaluating the effects of sample contact materials. Parker et al. (1989) indicated that only one contaminant (PDCB) was significantly sorbed on PTFE after 1 hour (8 % sorbed) compared with about 5% sorption on PVC. None of the other 9 contaminants were indicated to have significant sorption at 1 hour. After 8 hours maximum sorption of PDCB and MDCB on PTFE was 16%, with all other contaminants having less than 10% sorption. All PVC sorption at 8 hours was less than 5%. After 24 hours maximum sorption of PDCB and MDCB on PTFE was 22%, while all others were less than 15% adsorbed. All PVC sorption at 24 hours was less than 8%.

Both Reynolds and Gillham (1986) and Parker et al. (1989) concluded that there was little likelihood of sorption causing a significant problem for most analytes with contact periods of less than 24 hours. The results of the experiment of Sykes et al. (1986) also support this conclusion. Parker et al. (1989) indicated that PVC had less likelihood of significant sorption than PTFE. Research by Gillham and O'Hannesin (1990) indicated that after several weeks of contact, stainless steel effected no sorption of organic compounds studied. Flexible polyethylene and PVC exhibit almost immediate significant sorption of all analytes. Many analytes were more than 50% adsorbed in less than 24 hours, and all were eventually almost completely adsorbed. All rigid polymer contact materials tested exhibited eventual significant sorption of all analytes. However, none of the materials absorbed more than 10% of any of the compounds tested in 24 hours. In fact, most did not absorb more than 10% in 100 hours.

Parker et al. (1989) noted that despite general observations favoring PVC, individual interactions between contact materials and contaminants should be considered in selection of materials. While Reynolds and Gillham (1986) did not state a preference of contact materials based on their results, their data indicated that one contaminant (tetrachloroethylene) exhibited highly significant (50%) sorption on PTFE within 8 hours. PTFE was not tested by Miller (1982), but in his work tetrachloroethylene appeared to be the most completely adsorbed contaminant on PVC, polypropylene, and polyethylene. Tetrachloroethylene seems to have a strong sorptive tendency on many contact materials. Thus, property's of individual contaminants and their interactions with contact materials must be considered.

Preconditioning

Many have argued that because sample well water has been in contact with the casing for the period of time preceding sampling, the casing is in an approximate state of equilibrium with the well water. The experiment of Sykes et al. (1986) included a period of preconditioning with spiked water to simulate this condition. The results of Sykes et al. indicated that no significant sorption was measured within 24 hours for a preconditioned

PVC material. However, their experiment did not separate preconditioned from non preconditioned contact materials, and it cannot be stated with certainty that the insignificant sorption indicated is due to preconditioning rather than short material contact times.

Desorption

Once a contaminant is adsorbed to a contact material the process and rate by which it desorbs is an important consideration for many field procedures. For example, if it is suspected that a well used for sampling has in some manner been directly contaminated from the surface and must be cleaned out by purging, conditioning of the casing through sorption of the contaminants could effect the required duration and methods of cleaning. If the contaminant is easily desorbed in clean water, than the process of well decontamination could be rapidly accomplished by purging. However, if desorption is slow and gradual, a lengthy process of successive bailings and recoveries might be required. In some cases the well might be non recoverable for sampling purposes.

Similar considerations affect bailer decontamination procedures. A contaminant with little sorption should be easily cleaned with a water rinse. A contaminant with significant sorption, but a very rapid rate of desorption in contact with water should also clean easily with a water rinse. But a contaminant with significant sorption on the contact material but having a slow rate of desorption would tend to slowly feed low levels of contaminant into succeeding water samples. Decontamination with water would thus be a slow process and special cleaning procedures would be required.

The data of Parker et al. (1989) indicate that adsorption rate constants (K_a) and desorption rate constants (K_d) of tested contaminants on PTFE are significantly related at 0.01 probability (fig. 1), but that less than 50% of the predictive variability of the desorption constant can be accounted for with the adsorption constant. Parker et al. (1989) noted that the order of desorption rates tended to parallel those of adsorption. However, they observed that for PTFE, the two cases of greatest adsorption coefficients did not correspond with the largest desorption coefficients. Miller (1982) also observed that following six weeks of adsorption, tetrachloroethylene was completely adsorbed to PVC casing. After six

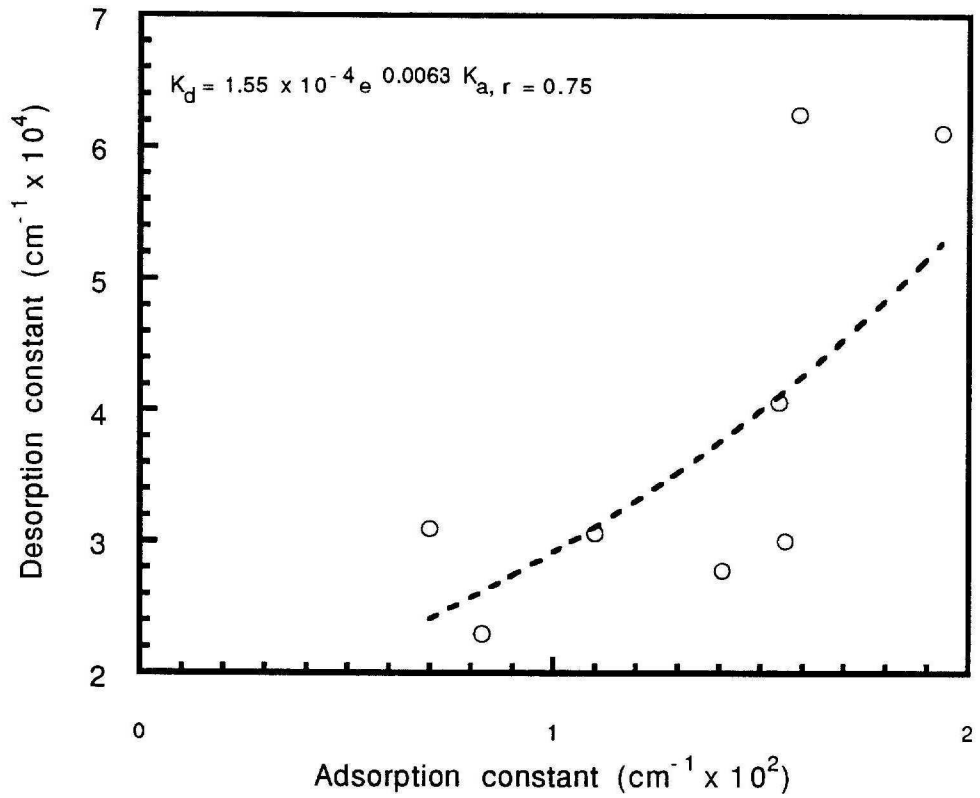


figure 1. Relationship between adsorption coefficient (K_a) and desorption coefficient (K_d) from data of Parker et al. (1989).

weeks of desorption, however, no desorption of tetrachloroethylene was observed.

Generally, it seems that desorption rate constants are much smaller (one to two orders of magnitude) than adsorption constants, but that more quickly adsorbed materials are also more quickly desorbed.

Generally Miller et al. (1982) found that both adsorption and desorption were least for PVC and greatest for polypropylene and polyethylene. Parker et al. (1989) observed no significant sorption of any contaminants on stainless steel.

Sorption Process

The tendency of a material to adsorb a specific contaminant is described as an equilibrium coefficient (K_{eq}), which is the ratio of K_a to K_d . Parker et al. (1989, 1990) found that K_{eq} for contaminant adsorption on PTFE was strongly ($R^2 = 0.98$) related to the log of the octanol-water partition coefficient (K_{ow}).

$$K_{eq} = 14.5 \log K_{ow} - 2.51 \quad (1)$$

No relationship was attempted for PVC because measured adsorption of contaminants was too small. K_{eq} is related to the equilibrium concentration of organic solute in aqueous solution after long term contact with the bailer or casing. However, Parker et al. (1989) point out that the speed of removal from solution is more dependent on K_a . They observed that for small planar molecules the K_a tends to be high, speeding sorption and removal from solution.

Parker et al. (1989) specified that eq. 1 applied primarily to hydrophobic substances, and that for hydrophilic substances, such as those having a tendency to hydrogen bond with water, eq. 1 would overestimate K_{eq} . Parker et al. also specified that adsorption of hydrophilic nitro-containing compounds would likely be overestimated by eq. 1. Thus, rapid decontamination of well casing or bailers with adsorbed contaminants would be most probable with hydrophilic chemicals, or chemicals having a small K_{ow} . Timely decontamination of hydrophobic materials having large K_{ow} would likely require use of an organic solvent.

Reynolds and Gillham (1986) compared the time for 10 % loss of an analyte from solution (labeled h_{90} for 90% remaining in solution) on PVC and PTFE to K_{OW} . Although they concluded that there was no apparent relationship, their data seems to indicate that a relationship between Log K_{OW} and contact time does exist in the lower K_{OW} ranges for both contact materials (fig. 2). On figure 2 the contact time for 1,1,1-trichloroethane was set at 5 weeks (although Reynolds and Gillham indicated > 5 weeks) so that the top charged value had still not reached 10% sorption. Still, even with a larger h_{90} , a trend is discernible. Moreover, PVC and PTFE sorption times seem to be similar from these data.

Published experiments all have limited ranges of solute concentration. The applicability of documented sorptive behavior and properties to other solute ranges depends on the process by which contaminants are sorbed on contact materials. For example, if the rate of sorption is non-linear (dependent on solution concentration) much lower rates of sorption could be expected for lower concentration ranges. Conversely, if sorption is preferential and if there are a finite number of sorption sites, then one might expect threshold behavior in which all solution contaminants would be adsorbed until sorption sites are satisfied, after which no further sorption (or desorption) would occur. In this case, at small concentrations all of a contaminant might be adsorbed to the contact material giving a false nondetection.

Reynolds and Gillham (1986) tested a model based on absorption and dissolution of contaminants on and into a contact material. Their model is

$$\frac{C}{C_0} = \exp\left(\frac{[KDt]}{A^2}\right) \operatorname{erfc}\left(\frac{[KD]^{1/2} t^{1/2}}{A}\right) \quad (2)$$

where C is solution concentration ($\mu\text{g/L}$) at time t (sec), C_0 is initial solution concentration, K is the partition coefficient for the contaminant between the solution and the contact material (dimensionless), and D is the diffusion coefficient in the contact material (cm^2/sec). Eq. 2 describes a process that is linear and non preferential (there are no specified threshold boundary conditions). According to eq. 2 the rate of sorption

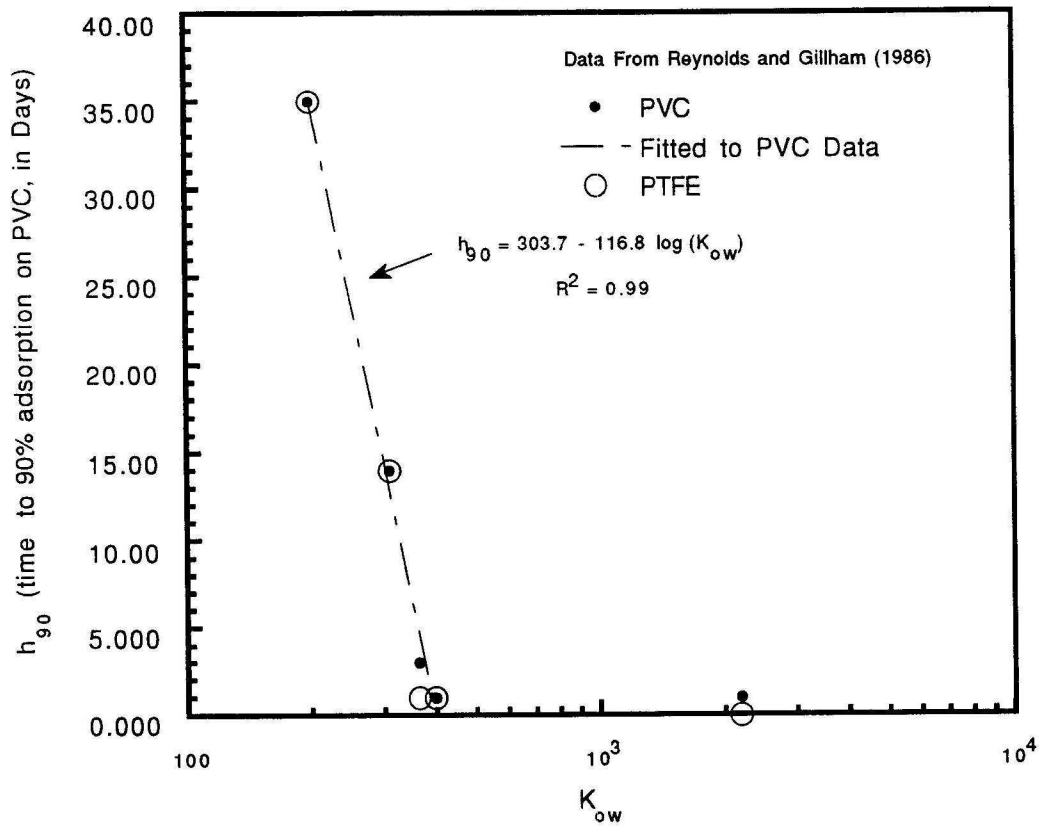


figure 2. Relationship between time to 10% removal of an organic substrate from solution (h_{90}) and the octanol/water partition coefficient (K_{ow}) from data of Reynolds and Gillham (1986).

is exponentially dependent on K and D properties for the contaminant and contact material, and the effective power of K and D are both multiples of contact time. In short, regardless of the sorptive properties of the material, if time of contact is sufficiently short, sorption (or desorption) should be negligible.

Most of the Reynolds and Gillham (1989) sorption data for solutes having concentrations of 20 to 40 $\mu\text{g/L}$ fitted well with eq. 2. The exponential sorption over time indicated by Miller (1982) for data in the 2 to 5 $\mu\text{g/L}$ range also tends to support the validity of a model similar to eq. 2. In both cases lack of nonlinear dependency on C indicates that extrapolation to lower solution concentrations is promising. However, conclusive and direct evidence of non preferential and non threshold sorption on contact materials in the sub $\mu\text{g/L}$ range is still needed.

Factors Affecting Sorption

Parker et al. (1989) have stated that less sorption would be likely for compounds having hydrophilic tendencies. Nitro-containing compounds were stated as likely examples. However, the hydrophilic tendency of some nitro compounds (including triazines forming the base of RDX) are pH dependent. Such compounds, even with large K_{OW} , would likely tend to adsorb less on PTFE (and possibly other materials) when in solutions having higher pH.

Parker et al. (1989) have observed that corrosion of stainless steel caused by exposure to salty water did not influence the sorption or desorption of organic compounds. Miller also noted that the presence of metals (lead and chromium IV) in solution did not influence sorption of organic compounds.

Analytical Interference and Spurious Detections

Stability of contact materials, and the possible leaching of substances that might cause analytical interferences or spurious detections in samples taken from waters in contact with them, is a concern in their selection and treatment. The considerable published work documenting leaching of plasticizers from flexible PVC and solvents from solvent weld glues used to bond PVC pipe has been reviewed by Parker et al. (1989). For stainless steel

tubing, leaching of iron has also been documented and reviewed by Parker et al. (1990). Hewitt (1992) reported that both sorption and leaching of several trace metals were significantly larger for stainless steel than for PTFE. PVC leaching and sorption of metals were generally larger than PTFE, but the difference was seldom statistically significant. Because of metal compounds used in production of PVC, cleaning of casing before placement has been recommended by Parker et al. (1989).

Despite these indications of possible problems, most evidence indicates that leaching effects on analytical interference and spurious detection are minimal for rigid (non plastic) PVC assembled without solvent weld glues (threaded joints). Neither Parker et al. (1989) nor Curran and Tomson (1983) found analytical interferences from samples in contact with rigid PVC. Also, Miller (1982) found no evidence of plasticizers or other leachate that could cause analytical problems.

Literature Review Summary

Comparing sample contact materials including polyethylene, polypropylene, rigid PVC, stainless steel, polyvinylidene fluoride, epoxy-impregnated fiberglass and PTFE, the best contact material for dilute organic contaminants from the standpoint of sorption appears to be stainless steel. Rigid PVC is least sorptive of all of the polymer contact materials tested, including PTFE. Flexible polymers, including polyethylene and flexible PVC, are highly sorptive, and do not make good sample contact materials. Stainless steel, however, may leach iron and other metals (Parker et al. 1990, Hewitt 1992). Polyethylene, polypropylene, and PVC adsorb lead.

There does not appear to be a significant organic contaminant leaching problem with any of the materials (including rigid PVC) provided solvent weld glues are not used to bond joints. After sufficient time leaching from solvent welded joints might also become negligible, so that old monitoring wells would cause minimal problems in sampling for organic compounds. For both sorption and desorption the time of contact with the bailer or casing is an important factor.

Research has indicated that for most organic compounds, and for procedures involving small sample contact times (<24 hours), the use of PVC in sampling organic compounds is not a significant factor. There are exceptions, however, and knowledge of interactions of specific contaminants and contact material would be desirable and advisable for monitoring programs.

Where project specific or compound specific information is not available, some clues concerning adsorptive behavior can be discerned from physical and chemical properties of contaminants. The octanol/water partition coefficient and hydrophilic properties of the contaminant appear to be strongly related to adsorptive tendencies, which should affect sample integrity, effectiveness of cleaning procedures, and likelihood of cross contamination of wells. Generally, larger sorption and slower desorption would be expected from chemicals having a larger K_{OW} , and less hydrophilic characteristics. Lesser suitability of water wash procedures alone, would also be expected for compounds having larger K_{OW} and less hydrophilic characteristics. Diffusion rates of organic compounds in a given contact material could also influence the effectiveness of bailer cleaning methods. More work is necessary to demonstrate that sorption and desorption are linear processes at lower (sub $\mu\text{g/L}$) concentration levels.

METHODS

In August, 1992, four shallow wells (screen intervals between 15 and 30 feet) were chosen on different sites in Ransom County, southeastern North Dakota, for evaluation of the effectiveness of distilled water (DW) rinse alone in cleaning a PVC bailer after contact with a known concentration of pesticide. One of the wells was in a shallow semi-confined aquifer. Three were placed in shallow unconfined aquifers. Six 3 liter water samples were taken at each well site. These included (1) an initial background well-water sample; (2) a spiked deionized water sample placed in contact with a PVC bailer for approximately one minute; (3) a distilled water (DW) sample taken after bailer contact,

and following one thorough DW rinse of the bailer; (4) a DW sample taken after bailer contact, following multiple thorough DW rinses of the bailer after the spiked sample; (5) a well-water sample taken with the same bailer from the same well as sample (1) following the multiple DW rinse and 15 additional bails from the well; and (6) a control sample of spiked deionized water taken directly from the field sample container.

Initial contaminated spikes (sample 6) consisted of two different initial concentrations, labeled (Low and High) for six pesticides which included bromoxynil, diclofop-m, dimethoate, methyl parathion, propiconazole, and trifluralin. Samples for each of the two initial treatments were taken on two replicates well sites. Treatments are summarized in table 1. Initial spike concentrations and field data are summarized on table 2. Each of the wells used for sampling were constructed of 2 inch (5.1 cm) rigid PVC pipe, with five foot (1.5 m) 18 slot well screens. Each of the wells had been constructed during 1989 and 1990 (at least two years prior to the experiment). Casing and screen joints were secured using stainless steel screws on three of the wells. Solvent weld glue had been used for securing well joints on one of the wells (table 1).

Preparation and Handling of Spiked Samples

Spiked deionized water for the Low and High treatments (table 1) were prepared by diluting samples of known analyte concentration the afternoon (< 24 h) before the beginning of field sampling, and were stored in 20 liter PTFE carboys at 4 degrees C. Spiked sample carboys were taken directly from the cooler at 8:10 A.M. on the morning of sampling, and were packed in ice in two open portable coolers. Each cooler and carboy was covered with two opaque nylon tarpaulins to protect the containers from light, and to help keep the carboys cool. Transport time to the first sample site was about 4 hours. Sampling began at 12:45 P.M. and was completed at about 8:30 P.M. During the field experiment the carboy not in use was kept cool and covered. The carboy in use was uncovered and placed for easy access only during the actual sampling time (about 1 and 1/2 hour) on each site. Each carboy was then covered and cooled during transport. Same treatments were used consecutively to minimize light exposure.

table 1. Summary of spike treatments and well locations used for sampling; and summary of field procedures used on each site, order of procedure (or treatment) application, and the Treatment Index (described in Methods section) used to evaluate each treatment.

Locations of Each of the Spike Treatments				Sample Procedures on Each Well Site		
Well Locations	Well Joints	Initial Spike Concentration	Order Of Well Sampling	Field Treatment Description	Treatment Index	Treatment Field Order
T134N R57W S18 CCC	SS Screws	Low	1	Initial Well Sample	0	1
T134N R58W S13 DCD	SS Screws	Low	2	Spike Sample	5	6
T134N R58W S34 ACBC	SS Screws	High	3	Spike Sample Exposed To Bailer	4	2
T134N R58W S29DAA	Solvent Weld Glue	High	4	Single Wash {1 DW Wash Treatments}	3	3
				Multiple Wash {> 6 DW Wash Treatments}	2	4
				Multiple Wash {Multiple Wash + 15 Bails}	1	5

table 2. Summary of experimental data. *Italicized values* indicate estimates of trace values, or values below the standard laboratory minimum detection level. L is low analyte concentration in the field spike treatment; H is high analyte concentration in the field spike treatment; Order of Sampling is the order in which samples were taken on each site; and Treatment Index is the ranking of treatment intensity described in the Methods section and in table 1. ND-MDL is the minimum detection level routinely reported by the North Dakota State Laboratory.

Treatment Concentration Levels	Well Order (Table 1)	Replicate Number	Order of Sampling	Treatment Index	diclofop-m [µg/L]	methyl parathion [µg/L]	trifluralin [µg/L]	MCPA [µg/L]	dimethoate [µg/L]	bromoxynil [µg/L]	propiconazole [µg/L]
L	1	1	1	0	ND	ND	0.004	ND	ND	ND	ND
L	1	1	2	4	3.720	1.93	3.09	13.5	0.10	1.3	3.87
L	1	1	3	3	0.034	0.006	0.087	ND	ND	ND	ND
L	1	1	4	2	0.013	ND	0.011	ND	ND	ND	ND
L	1	1	5	1	ND	ND	0.002	ND	ND	ND	ND
L	1	1	6	5	6.42	2.26	3.88	13.4	0.10	0.39	4.04
L	2	2	1	0	ND	ND	0.008	ND	ND	ND	ND
L	2	2	2	4	0.462	ND	0.31	ND	ND	0.33	0.39
L	2	2	3	3	0.028	ND	0.044	ND	ND	ND	ND
L	2	2	4	2	0.024	ND	0.017	ND	ND	ND	ND
L	2	2	5	1	ND	ND	0.006	ND	ND	ND	ND
L	2	2	6	5	2.07	2.36	1.34	11.5	0.10	0.47	3.59
H	3	1	1	0	ND	ND	0.028	ND	0.10	ND	ND
H	3	1	2	4	18.2	8.97	17.3	50.1	0.04	4.23	15.1
H	3	1	3	3	0.171	ND	0.228	ND	0.10	ND	0.04
H	3	1	4	2	0.086	ND	0.124	ND	ND	ND	ND
H	3	1	5	1	0.018	ND	0.008	ND	ND	ND	ND
H	3	1	6	5	17.0	8.32	14.6	49.2 49.2	0.4	4.15	13.7
H	4	2	1	0	ND	ND	0.019	ND	0.023	ND	ND
H	4	2	2	4	20.4	ND	14.0	55.5	0.20	3.62	10.1
H	4	2	3	3	0.018	ND	0.227	ND	0.008	ND	0.08
H	4	2	4	2	ND	ND	0.099	ND	0.002	ND	ND
H	4	2	5	1	ND	ND	0.01	ND	ND	ND	ND
H	4	2	6	5	0.566	7.43	13.8	41.3	0.200	ND 49.03	11.0
ND-MDL					0.05	0.01	0.055	2	0.01	0.1	0.02

Three workers were used for sampling on each site. The clean worker (CW) performed all tasks in direct contact with the water sample. These included holding, cleaning, and all other contact with the bailer. The CW did not touch wells, grass, soil, wash containers, bottles, or any other possible source of contamination during sampling. An assistant (AW) performed all tasks of direct assistance to the CW, including handling sample bottles, wash water and soap containers, and dispensing rubber gloves. The AW did not have direct contact with the water or bailers at any time, nor did the AW have contact with trash, soil, and known contaminated materials. A third utility worker (UW) was assigned to perform all work likely to cause inadvertent contamination. UW tasks included cutting or compacting grass around the sample well, preparing the work area, taking photographs, and handling trash.

Three vehicles were also used for sampling. The tailgate of the clean vehicle (CV) was used as a bench and work area for sampling. The back and tailgate of the CV was thoroughly cleaned with alkonox detergent and hosed with tap water the day before loading and transporting experimental materials. The back of the assistant vehicle (AV) was used to hold and store bottles sampled. The back of the utility vehicle (UV) was used to store trash and contaminated materials.

Field Sampling Preparation

The tailgate of the CV was covered with polyethylene, and the sample carboy was placed on the tailgate in a position for convenient dispensation of water. The general area around the sample well was prepared by the UW. Grass was compacted or cut around the well to avoid contact with the bailer, and a polyethylene skirt (about 1.5 x 1.5 m) was placed around each well. The top of the well, the cap, and the interior cap threads were wiped with a rag soaked in alkonox detergent by the AW. The outside of the cap was wiped first, then the inside of the cap and well. A work table was constructed of two stacked coolers, and covered with a clean polyethylene sheet on each site for filling bottles.

The cleaning procedure before sampling was as follows. (1) The UW washed the hands of the AW by pouring distilled water over them. (2) The AW then washed the hands of

the CW. (3) The AW removed the box of rubber (vinyl) gloves from a protective polyethylene bag (without touching the gloves) and held the box while the CW removed them by the edge of the palm and put them on. (4) The AW then rinsed the gloved hands of the CW with distilled water.

Sampling was initiated as follows. (1) The AW held the polyethylene bag containing the PVC bailer, and opened it. The CW removed the bailer. (2) The AW opened a polyethylene bag containing nylon rope and extended it to the CW without touching the rope or the bailer. (3) The CW uncoiled the rope, tied it to the bailer, and removed the bailer from the bag. (4) The AW removed the cleaned cap from the well, and the CW began bailing.

Field Sampling

For each site, six samples were taken. The purpose of each sample, and detailed sampling procedures are described as follows. A summary of indices used to describe spike concentrations and field treatments is on table 1. A description of each field sample in order of sampling is as follows.

Sample 1: Uncontaminated Well Sample

The purpose of Sample 1 was to determine the background levels of any of the spike contaminants in the four field wells used in the experiment on each site. Sample 1 was the first sample taken on each site. The well was bailed 30 times (except for Site 4 which was bailed 45 times) with a clean PVC bailer. This was the equivalent of approximately five well bore volumes. Cleaning of the bailer prior to use on each new site consisted of washing with alkonox solution, multiple rinses of distilled water, hexane, and acetone on the previous site, and a multiple distilled water rinse on the sampling site. The multiple distilled water rinse was used to wash away possible trace contaminants caused by interaction of hexane and acetone solvent with the PVC bailer in decontamination procedures used on the previous site.

The AW placed three bottles on the table, and opened caps briefly while the CW poured sampled water into the bottles. Each bailed sample was distributed over all three bottles, and the AW recapped each bottle immediately after completion of pouring.

Sample 2: Spiked Water Decanted Through Bailer

The purpose of Sample 2 was to simulate a contaminant sample after a short period of contact with a PVC container, either bailer or well casing. Spiked water was decanted into the bailer from the top until it began to overflow from the breather hole near the top. Spiked water was also poured over the outside of the bailer, and also over at least one foot of nylon rope nearest to the bailer. Usually some of the water was inadvertently poured over rope coiled in the hand of the CW holding it around the center of the bailer. Water was held in the bailer for 60 seconds to simulate the approximate period of contact time for water samples taken in a shallow well in a sandy or gravelly aquifer. Samples were distributed into three bottles as previously described for sample 1.

Sample 3: One Distilled Water Rinse

The purpose of Sample 3 was to simulate contaminant concentration in sample water after one wash with DW alone. Because up to six bailer fillings were required, it is actually a composite mixture of 1 through 6 rinses of the bailer. A similar number of dilutions would also occur in actual field sampling, however. DW was poured over the outside of the bailer (and gloved hands of the CW) by the AW for one thorough rinse. DW was also poured over the contaminated portions of the rope. The bailer was then filled with DW and water was agitated with shaking and rotational motions of the bailer, and then drained. After one thorough rinse, DW was poured into the top of the bailer, held for 60 seconds (with agitation and rotational movement as in the previous wash), and then decanted out the top into three sample bottles. Again, an even distribution of sample between the three bottles was attempted. While decanting the rope and rope connector were held back so that rope contact with sample water was minimized. After decanting each bailer sample, the outside of the bailer and rope were rinsed with DW. Each sample usually required a total of five, and sometimes six fillings with DW, depending on the seating of the ball in the bailer.

Sample 4: Six Distilled Water Rinses

The purpose of Sample 4 was to simulate multiple DW rinses prior to reuse of the bailer. Sample 4 was taken immediately after Sample 3. Samples were taken and decanted in the same manner previously described for Sample 3.

Sample 5: Twelve Distilled Water Rinses and 15 Bails of Well Before Well Sample

The purpose of Sample 5 was to simulate multiple rinses (a total of 12 including rinses from the taking of Sample 4) and also additional washing from minimal bailing of the next well. A total of 15 bails (approximately 2 to 3 well volumes) were made before sampling.

Sample 6: Direct Spike from Carboy

Sample 6 consisted of a direct spiked sample of known concentration poured from the carboy into the sample bottles. This was the check for the experiment.

After completion of sampling on each site, contaminated rope was removed from the bailer and discarded, gloves were changed, and the bailer was cleaned with alkonox detergent and rinsed with distilled water at least three times. The bailer was then disassembled and rinsed with hexane and acetone, allowed to dry, and then rebagged. The bag with bailer was placed in a 6 inch PVC pipe holder and protector. The site was cleaned. Trash, including all plastic covers and bags) was put into the utility vehicle. Spiked carboys were put back on ice and covered for movement to the next site.

Sample Handling

Sample water was stored in one liter solvent cleaned tinted glass jars. All water samples were kept in the dark and transported on ice in coolers on the same day of sampling to a holding refrigerator, where they were kept at approximately 4 degrees C overnight. They were transferred from the holding refrigerator on ice to the North Dakota State Consolidated Laboratory on the following morning, and were stored at 4 degrees C.

Extractions were made within 7 days of sampling, and analytical determinations were made within 30 days of sampling.

Laboratory Methods

Analytes methyl parathion, propiconazole, trifluralin, dimethoate, and diclofop-methyl were analyzed using a Hewlett Packard Model 5890 gas chromatograph (Restek Rtx-35 and J&W DB-5 columns) according to EPA method 508.3 (USEPA 1990). Analytes were extracted first with methylene chloride and then with hexane. MCPA was analyzed using a Hewlett Packard model 5890 gas chromatograph (equipped with a DB5.625 column) coupled with a Hewlett Packard 5970 mass spectrometer, according to EPA method 515.1 (USEPA 1990). Bromoxynil was analyzed using high-performance liquid chromatography according to the method of Brown et al. (1984) with a Supelcosil LC-18 25 cm x 4.6 mm analytical column and a Supelcosil LC-189, 2 cm x 4.6 mm Guard column. Bromoxynil was injected directly in the sample-water matrix. Further information and conditions of analysis are available upon request.

Reporting Procedures

The standard MDL values for the ND Health Department Lab (ND-MDL) are based on the lowest analyte standard routinely run by the laboratory with water samples. A low standard is run with each group of approximately 10 samples. If a detection is made, samples with detections (and the low standard) are then run on a second chromatographic confirmation column. If detections are still made, then a full range of standards are run to provide a precise quantitative calibration for the sample set. While the low standards are routinely run with proficiency, the reported ND-MDL is based upon EPA requirements for routine water analysis rather than actual local limits of analytical capability. With each set of samples a surrogate spike is run (Mirex [Dodecachlorooctahydro-1,3,4-methano-2H-cyclo-buta(cd)pentalene] for base neutrals and 2,4-DB [4-(2,4-dichlorophenoxy)butyric acid] for acid extractions). Standard spike recoveries of 70 to 130% are considered to be

normal. Greater or smaller surrogate recoveries are considered to be indicators of possible interferences or synergisms.

Where laboratory MDL levels are statistically determined, the null hypotheses is most frequently defined so as to minimize the probability of false detections (errors of the first kind) due to laboratory error in an independent sample. In some routine environmental monitoring this is the most reasonable approach. However, our concern in this experiment is with the efficacy of distilled water cleaning, and with the possibility of cross contamination between wells caused by adsorbed contaminants on the bailer (false detections due to bailer contamination). In order to achieve a higher level of certainty of cleanliness due to field methods, we are more concerned with laboratory errors of the second kind (false non detects), which would invalidate our conclusions concerning the assurances of cleanliness on the bailers. For this reason, we asked that chemists report, to the best of their ability, analyte spike values which they deemed to be detectable at below standard ND-MDL. This information is reported with the intention of providing additional assurance where non detects are claimed following cleaning. This information, while quantitatively less certain, might also be useful as a clue concerning possible problems that might be encountered for laboratories or future applications employing methods having lower detection levels than those reported here.

While recognizing the uncertainties that enter into analysis with below MDL reporting, we believe that the certainty of detection is enhanced by the fact that sample treatments are not independent and by the simplicity of the deionized water (and later distilled water in the field) matrix. Certainty of detection is enhanced because each analyte is known (through introduction) to be a part of the spike solution applied to the bailer before cleaning. Each successive cleaning procedure is then an operation performed on a previously known detected presence (or absence) of the analyte. The graduated change in reported detections provides an interpretive context which enhances confidence in the indicated analyte presence, compared with a random and independent analysis. The use of a deionized water and DW matrix, with no spurious contaminants, also enhances confidence in the uniqueness of detections, compared with a random sample of natural water where other

unknown contaminants may persist. There does remain the possibility of exudates from the bailer and of possible interferences or synergisms.

The above explanations apply only to DW treatments (table 1) which are the spike and wash samples. They cannot be applied to initial and final well samples, in which supporting information of known presence is not held. The authors would be very reticent to treat sub ND-MDL detections reported in this paper as reliable indicators of environmental contamination. The sub ND-MDL values are reported for initial and final well samples only as indicators of their possible effect on later spike and cleaning treatments, since treatment 1 was the first sample taken in each field procedure application.

Laboratory Data Evaluation

Some difficulties were incurred in laboratory procedures that require further assessment of data reliability. These difficulties include (1) low or high recoveries on some Mirex surrogate spikes, and (2) low recoveries on certain analytes. Values for (A) Mirex surrogate spikes and (B) sample spike recoveries of concern are shown on table 3. Both surrogate spikes and analytical spike recoveries may or may not indicate problems in sample analyte recovery. There remains a possibility that laboratory analyte, matrix, or treatment of the blanks may have caused the poor apparent recoveries. Fortunately, in this experiment we have one additional check for laboratory procedures in the original mixed field dilution samples (which were mixed to a known initial concentration) .

While the desirable range of surrogate spike recoveries is usually between 0.70 and 1.30, some surrogate blanks exceeded this range. The mean recovery was 0.91, the median was 0.85, and standard deviation was 0.33 (for 25 samples). The surrogate recovery range was 0.46 to 1.85. Known initial dilution concentrations of field samples were plotted against corresponding surrogate recovery values (fig. 3) to see if any trend could be found in the data. The dependent variable (C/C_{FS}) is the fraction of measured field dilution samples (both before and after bailer contact) to known initial sample dilution concentration, as planned and mixed. No trend could be discerned, which indicates that the problem was likely with the surrogate samples themselves.

Similar analysis was made for field dilution data and laboratory sample spikes. Of particular concern were dimethoate and diclofop-m, for which low sample spike recoveries were observed. The results (fig. 4) indicate that for laboratory spikes having fractional recoveries greater than 0.5, there was a good correlation between field sample recovery using initial dilution concentration as a reference (C/C_{FS}) and laboratory sample recovery (C/C_{LS}) as represented by spiked laboratory samples (C_{LS}). There was also a good correlation for dimethoate, indicating that low concentrations measured in the lab were probably accurate indicators of low recoveries from field samples as well. However, C/C_{FS} for diclofop-m indicated that analytical results for field samples corresponded well with known initial dilution concentrations (on fig. 4 C/C_{FS} is between 0.8 and 1.1), and were thus poorly represented by laboratory spike recoveries. Only one value for diclofop-m indicated correspondence with the laboratory spike. Thus, laboratory spikes served as good indicators of recovery efficiency, except for diclofop-m which exhibited good recovery efficiency on field samples, but had poor recoveries in laboratory blanks. Of all samples, only dimethoate had recovery levels that were consistently unacceptably low.

Treatment Index

For purpose of comparison, an index of treatment intensity was devised. Each field treatment was assigned a number in order of logical expectation of cleanliness. Numerical ranking was from 0 to 5, with 0 representing no bailer contamination (well water alone); 1 representing the treatment of multiple DW washes and fifteen bails of the well; 2 representing multiple DW washes alone; 3 representing a single DW wash alone; 4 representing the spiked sample decanted directly from the bailer; and 5 representing the spike sample taken directly from the PTFE carboy. This index was used to order comparisons of treatment results.

table 3A. Laboratory surrogate (Mirex) spike recovery fractions for each field sample. C = field spike concentration treatment (1=Low, 2=High); R = field spike treatment replicate; T = bailer decontamination treatment number (from table 1).

Surrogate Spike (Mirex) Recovery Fraction								
First Sample Set			Second Sample Set			Third Sample Set		
C/R/T	recovery	Comments	C/R/T	recovery	Comments	C/R/T	recovery	Comments
Blank	.85		Blank	0.90		Blank	0.97	
Spike	1.11		Spike	0.82		Spike	0.84	
1-1-1	0.62		1-2-5	0.65				
1-1-2	0.91		1-2-6	0.85		2-2-3	0.74	
1-1-3	1.13					2-2-4	0.74	
1-1-4	0.94		2-1-1	0.89		2-2-5	0.67	
1-1-5	0.50		2-1-2	0.46		2-2-6	0.94	
1-1-6	1.13		2-1-3	0.72		2-2-6	0.69	duplicate
			2-1-4	0.80				
1-2-1	0.56		2-1-5	0.48				
1-2-2	0.88		2-1-6					
1-2-3	0.85			0.80				
1-2-4	1.59	interference	2-2-1	1.26				
1-2-4	1.26	duplicate	2-2-2	1.85	interference			

table 3B. Laboratory blank spike recoveries for selected analytes.

Analyte Sample Spike Recovery Fraction			
Second Sample Set		Third Sample Set	
analyte	recovery	analyte	recovery
trifluralin	0.69	trifluralin	0.70
dimethoate	0.20	dimethoate	0.06
methyl	0.81	methyl	0.84
parathion		parathion	
propiconazole	0.61	propiconazole	0.43
diclofop-m	0.25	diclofop-m	0.02

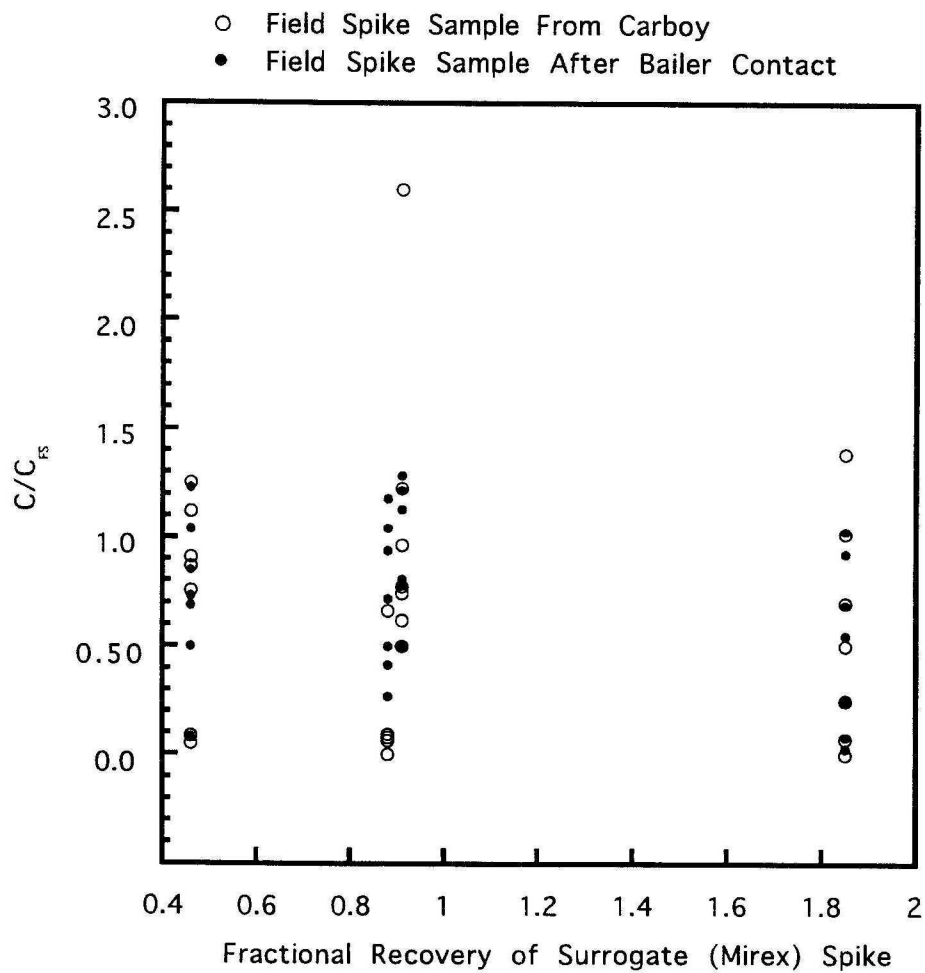


figure 3. Comparison of fractional recovery of all pesticides in field spike samples (using planned dilution concentrations [C_{FS}] as a reference) and fractional recovery of corresponding Mirex spikes.

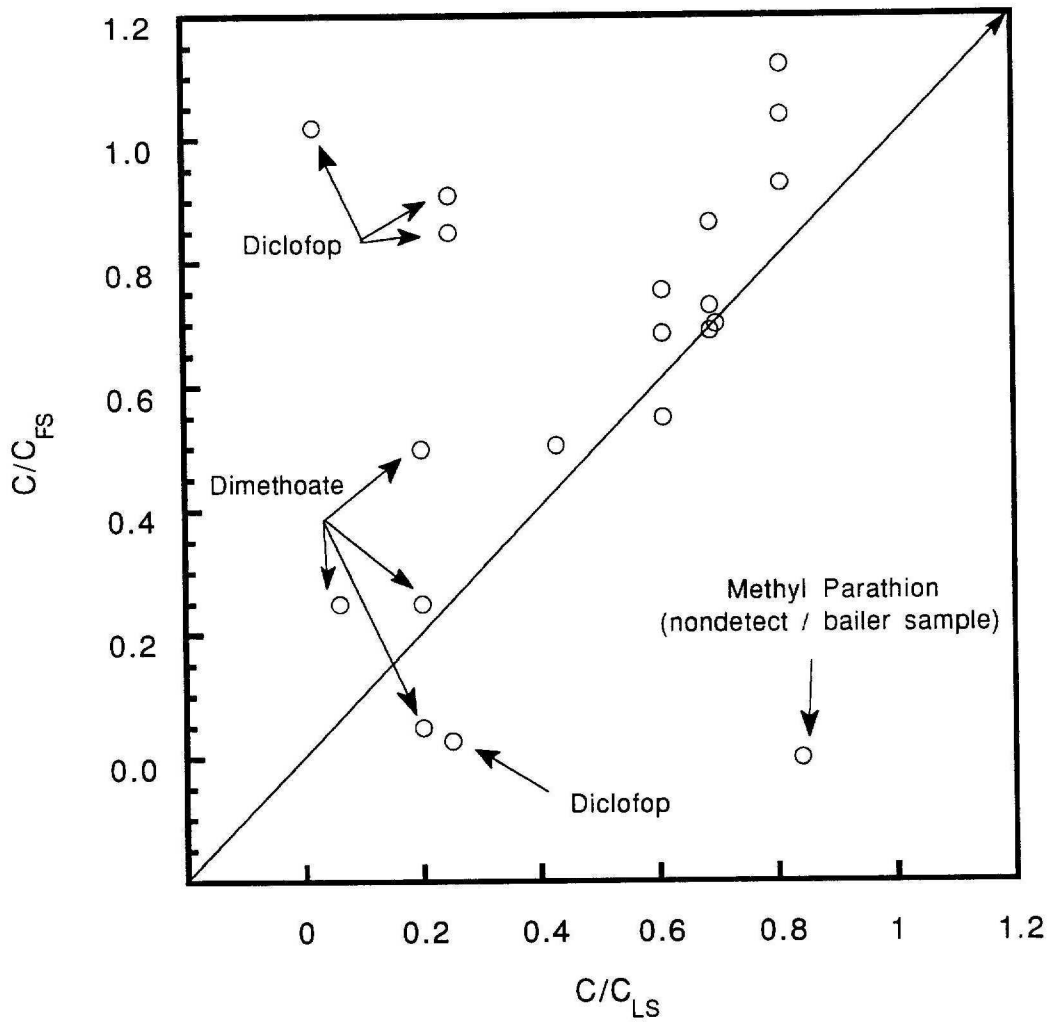


figure 4. Comparison of fractional recovery (C/C_{FS}) of field spike samples using planned dilution concentrations (C_{FS}) as a reference and fractional recovery of laboratory spikes (C/C_{LS}).

RESULTS AND DISCUSSION

Effect of Short Term Bailer Contact on Measured Analyte Concentrations

Measured spike concentrations, detected analyte concentrations after holding in the PVC bailer for approximately 60 seconds, and ND-MDL values are shown on table 2. All initial spike levels are above ND-MDL. To broadly assess the likelihood of interference or adsorption from the PVC bailer, measurements from the bailer samples were plotted against initial spike concentrations (fig. 5). Plots are repeated on linear and logarithmic scales. The arithmetic scale best represents data in the range of 1 to 60 $\mu\text{g/L}$, and also is capable of including non detect (0 $\mu\text{g/L}$) data which occurred on some of the bailer samples. However, the arithmetic scale fails to adequately represent the data in the range between 0.01 $\mu\text{g/L}$ and 1 $\mu\text{g/L}$ which form compact groups around the 1 to 1 identity line. Because of low analyte concentration values, deviation in this range is masked by the larger deviations in the upper ranges. Conversely, the logarithmic plot better illustrates and tests the agreement of spike and bailer values for the whole range of estimation. However, lack of correspondence of samples due to non detects cannot be evaluated using the log transformed data.

Because of heterogeneity of variance on the non-logarithmic data, the log data provides the most reliable assessment of probability for the slope evaluation. Visual inspection of the linear data (slope = 1.11), and slope tests of the log transformed data for the logarithmic plot (slope = 0.99, $s_b = 0.14$, $DF = 22$) indicated that the hypothesis that bailer concentrations would be generally less than spike samples because of adsorption was not supported at 95% confidence. A paired t-test also indicated that there was no significant difference between the spike sample and the bailer contact sample (although the spike sample mean was slightly smaller).

Analytes varying in specific replicates and treatments from the 1:1 relationship did not do so consistently. For example, two MCPA bailer samples were in good 1:1 agreement with spikes, one was a non detect (low), and the other was high (graph A of figure 5). There was no consistent pattern of variance by treatment (initial concentration of the spike) or

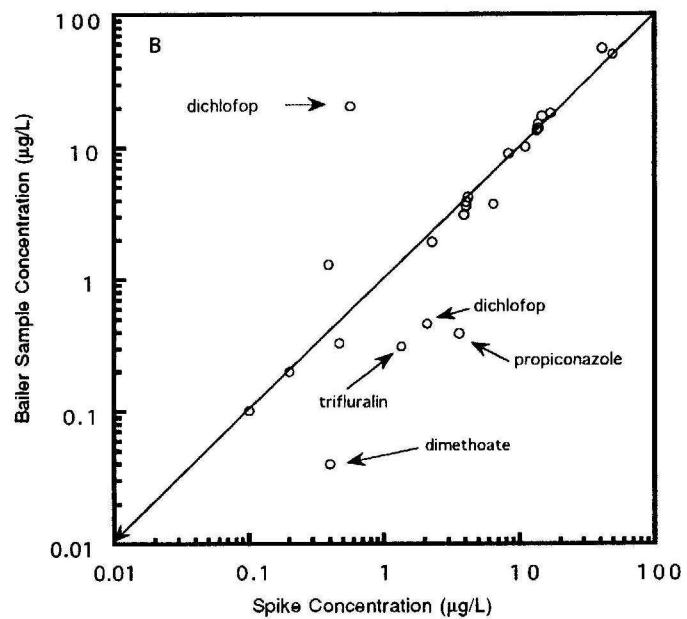
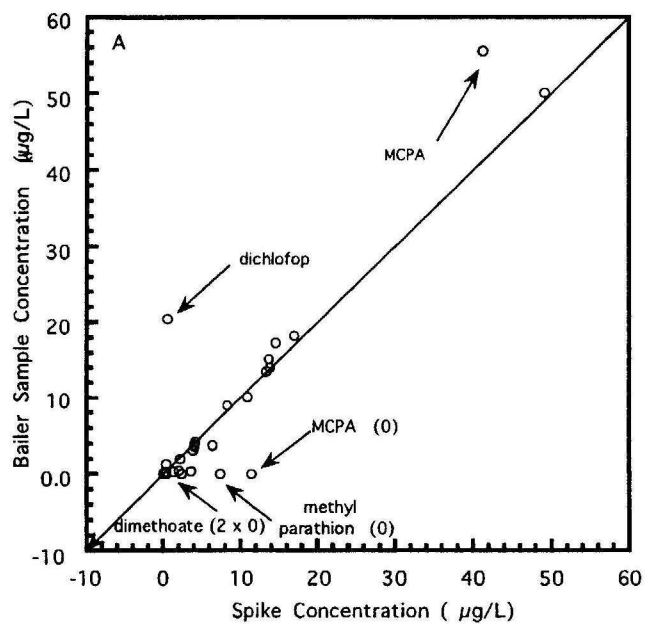


figure 5. Comparison of analyte concentrations from spiked deionized water before and after contact with a PVC bailer.

replicate. Two diclofop-m values were close to the 1:1 line on the log plot. Of the other two samples one diclofop-m value was high and the other low. There was no discernible pattern indicating sorption. Methyl parathion had three values in good 1:1 correspondence, and one non detect. Propiconazole and trifluralin measured values were slightly low for one replicate each. There were two non detects for dimethoate after decanting from the bailer. However, there was a problem in the laboratory with inadequate surrogate spike recoveries and the quality of the dimethoate measurements is questionable.

The source of deviation from agreement cannot be specifically identified (field or lab). However, overall deviations for comparisons of spike and bailer samples were random, rather than systematic, and the deviation from agreement was most marked in the lower concentration ranges.

Effect of Decontamination Treatments on Measured Analyte Concentrations

Of the initial ground water samples taken to determine the background contaminant levels, two pesticides were indicated as possible initial contaminants. These were dimethoate and trifluralin. Of these, only dimethoate was found initially in the ground water at levels above ND-MDL, and this in two of four samples taken (figures 6a and 6b). However, after contaminating the bailer, multiple rinses with DW, and bailing the well an additional 15 times, no detections of dimethoate were made in the well. Because of the care taken in field procedures, because other spiked analytes were not detected in well samples, and because of the order of sampling (first small concentration spike, then large concentration spike) direct contamination of the sample well by experimenters on site is not considered likely. It is possible that some direct contamination of the well might have occurred through the breather hole in the cap causing very localized contamination, and that additional purgation of the well effectively eliminated the contamination. Low spike recoveries for dimethoate on one of the wells for which initial detections were made indicate that laboratory error may have occurred. This, however, is speculative. Observation indicates only that neither detection was confirmed by a second sample taken within two

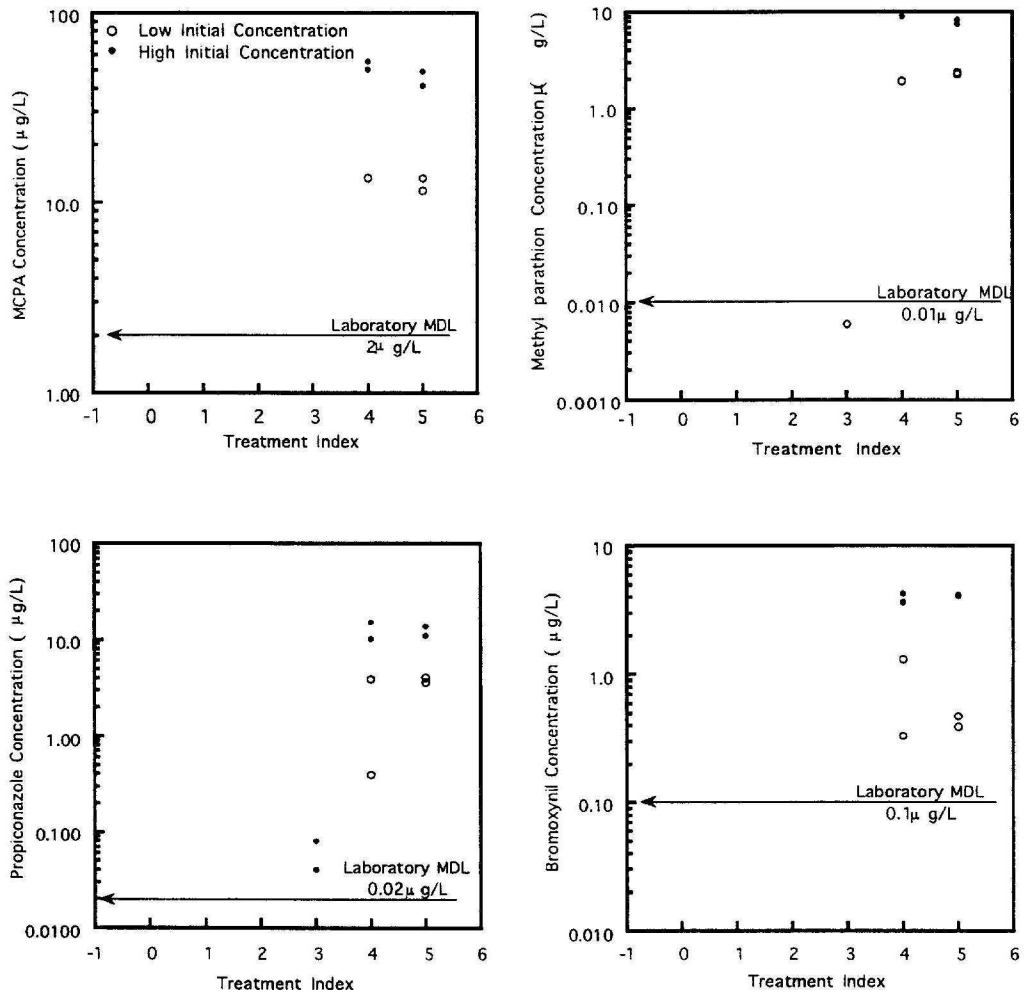


figure 6a. Concentration of samples for MCPA, methyl parathion, bromoxynil, and propiconazole for each cleaning treatment intensity.

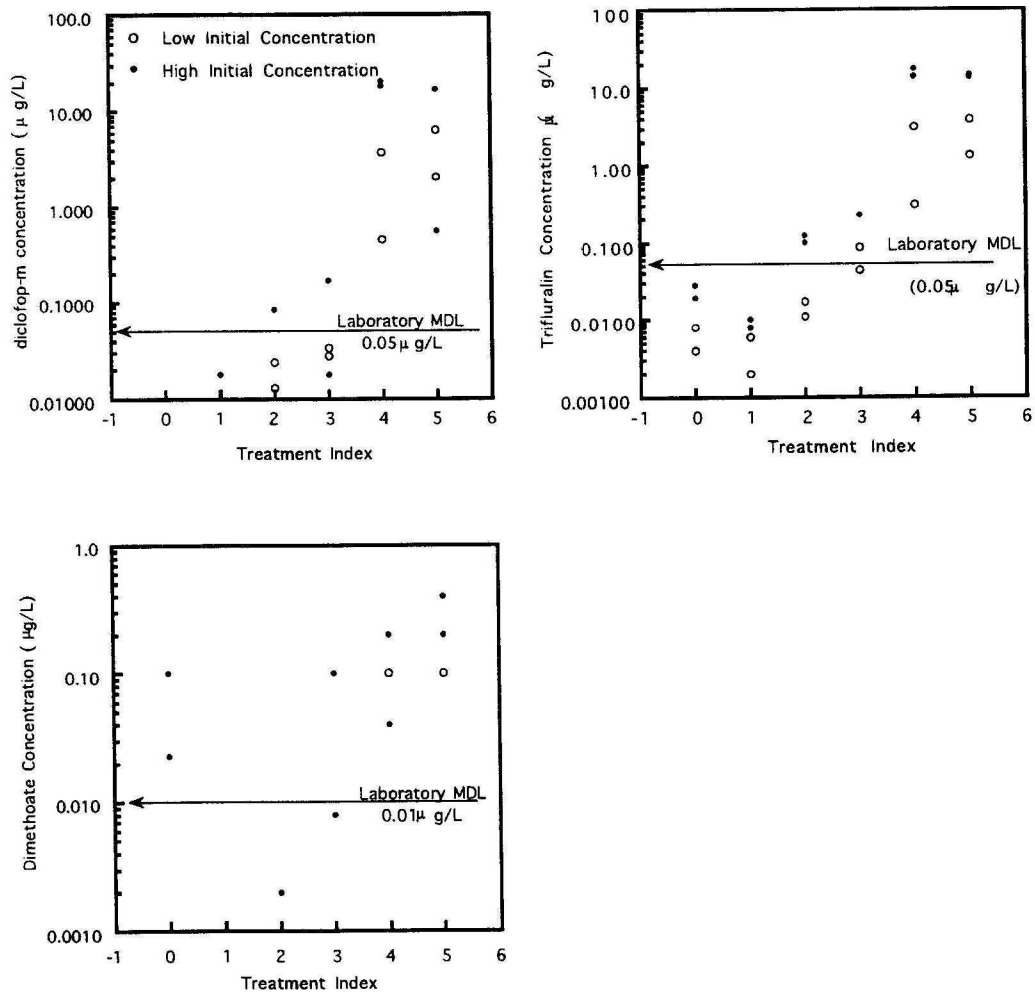


figure 6b. Concentration of samples for diclofop-m, dimethoate, and trifluralin for each cleaning treatment intensity.

hours of the first sample. Absence of detections may be related to low dimethoate sample spike recoveries indicated for dimethoate in some samples.

The possible (below ND-MDL) detections of trifluralin in the initial well samples are also presented with caution. Interpretation of these data is not assisted by the known presence of the contaminant on the bailer and the discernible trends of decreasing concentrations which enhances confidence in uniqueness of detections in the progressive wash samples. Rather, the initial well samples must be considered as a random sample, and the confidence level for detection is thus lower than that provided by the ND-MDL.

For trifluralin there remained indications of presence on the bailer after multiple DW washes and 15 additional bails in the well. However, all detection levels indicated were lower than those of the initial well samples by about one half order of magnitude. It is uncertain whether the contaminant source was residual from the spike decanted through the bailer, or a more dilute replication of the trace detections in the initial well water sample. Because trace observations are below laboratory ND-MDL these data should not be considered as a reliable indicators of an actual preexisting contaminant in the aquifers represented by these wells.

Of the seven contaminants tested, all were indicated to be below ND-MDL after multiple DW washes, and after 15 additional bails from the test well (figures 6a and 6b). None would have indicated contaminants from a previous well. Both diclofop-m and trifluralin, however, were indicated to pose some risk of cross contamination at higher initial contamination levels using multiple DW wash procedures without the additional 15 bailings of the well. Without additional bailings, likelihood of cross contamination was less for the lower initial contaminant levels. However, persistence of indications of trace presence at lower initial contaminant levels indicates that some error might still result from cross contamination caused by lower initial contaminant levels as well.

For dimethoate, multiple DW rinsings resulted in all samples testing below ND-MDL. One possible trace detection was indicated for the larger initial contaminant concentration without the additional 15 bails. The trace detection level, however, was

almost a full order of magnitude below the ND-MDL. Because of small laboratory sample spike recoveries all interpretations of dimethoate decontamination efficiency are suspect.

Four of the seven spike contaminants tested were indicated to be effectively cleaned from the bailer by as little as one DW wash (figures 6a and 6b). For MCPA and bromoxynil there was no indication of remaining contamination, either above ND-MDL or on the less certain trace level following a single thorough wash with DW. This applied to both initial spike concentration levels. Bromoxynil and MCPA appear to be effectively cleaned from the PVC bailer using a DW wash alone. For methyl parathion, there were no detections above standard laboratory ND-MDL following a single DW wash. However, there was one indication that some possible residual low level contamination may have remained after one DW wash for one of the low concentration contaminant spikes. No indicators of possible contamination persisted for the multiple DW decontamination procedure.

Propiconazole was indicated to have remaining contamination after one DW wash for the higher initial spike concentrations. However, no detections were made for the lower initial spike concentrations following one DW rinse, and no detections were made for any initial spike concentration following multiple DW rinses.

Even for cases where decontamination using DW wash procedures was incomplete, and where some degree of trace residual contamination remained, DW wash alone resulted in very substantial cleaning. With the exception of dimethoate, all other contaminants and treatments were indicated to have decontamination efficiencies of 98% or better from one DW wash. From multiple DW washes decontamination for all samples (including dimethoate) exceeded 99%. These cleaning efficiencies may be of assistance in interpreting the risk of cross contamination of wells, where the suspected contaminating well is known to have yielded a contaminant detection only slightly above MDL. These data would indicate that multiple washes for all analytes tested would be expected to decrease concentration levels by about two orders of magnitude.

Solubility and Partitioning Properties as Indicators of DW Cleaning Effectiveness

Because of the expense of analysis for organic constituents, clues for cleaning effectiveness based on commonly available physical or chemical properties and parameters would be useful. Two properties commonly examined are (1) the water solubility (S) and (2) the octanol/water partition coefficient (K_{OW}) of the analyte.

Parker et al. (1989) indicated that the equilibrium adsorption coefficient (K_{eq}) for organic contaminants was strongly correlated with $\log(K_{OW})$ for PTFE. Because $K_{eq} = K_a/K_d$ where K_a is the adsorption coefficient and K_d is the desorption coefficient, their findings indicate that analytes with greater tendency to partition into octanol have a larger tendency to adsorb on PTFE, in relation to their tendency to desorb. Parker et al. reported that PTFE had a much larger tendency to adsorb organic contaminants than did PVC. Moreover, they did not examine the relationship between adsorption on PVC and K_{OW} , because of the smaller levels of adsorption. Parker et al. (1990) did not find a significant correlation for adsorption with water solubility (although they did report that hydrophilic characteristics altered the predictive relationship between K_{eq} and K_{OW}). The combined work of Reynolds and Gillham (1986) and Parker et al. (1990) does seem to indicate that as a general rule, a larger tendency to partition into octanol serves a clue that the tendency to adsorb on some materials (as indicated by final equilibrium adsorption) is larger, and that the time required for adsorption of a given quantity of contaminant is less. The data of Reynolds and Gillham (1986) indicates that this applies to PVC as well as to PTFE (figure 2).

This experiment differs from those of Reynolds and Gillham (1986) and from Parker et al. (1989) in that it deals with the retention of small quantities of contaminant on the PVC after a very small contact time (approximately 1 minute), and release of that retained contaminant in successive washes having very short contact times. Nonetheless, retention of contaminants on a contact material surface is a function of adsorptive properties of the contaminant and the contact material, and the effectiveness of cleaning with DW should be a function of adsorptive and desorptive properties of the contaminant and the contact material.

Solubilities used (table 4) are from the Royal Society of Chemists (1990), and are based on a range of temperatures between 20 and 27 degrees C. Our results indicate (fig. 7) that with the exception of dimethoate, contaminant water solubility provides a reasonably good indicator of the effectiveness of DW washing. One DW wash appeared to be effective for all contaminants having a water solubility of at least 500 mg/L at approximately room temperature. An approximate decreasing power function relationship between desorbed contaminant concentrations in wash water following wash treatments and water solubility was observed. Multiple DW washes (> 6 DW washes) appeared to effectively decontaminate the bailer for all contaminants having water solubilities of at least 50 mg/L (with dimethoate being an exception). As with the single wash, a general power function relationship could be used to fit desorbing contaminant concentrations. Again, dimethoate was an exception. For multiple DW rinses and the additional bailing regime, all contaminants having a solubility of at least 50 mg/L were effectively removed from the PVC bailer. A power function with slope similar to the single DW treatment fitted well with the data. Non detects were based not only on ND-MDL criteria, but on all "possible" trace detections above laboratory analytical background "noise".

The K_{OW} value also appears to be related to effectiveness of DW wash regimes, again with the exception of dimethoate (fig. 8). Data used and sources for K_{OW} values are shown on table 4. Following one DW wash, a conservative threshold K_{OW} of 200 was observed. Below $K_{OW}=200$ no residual contaminant was noted following one DW wash. Above $K_{OW} = 200$ the percent of the original water concentration remaining in wash water was exponentially related to K_{OW} . For multiple (>6) DW washes, a similar relationship occurred, with the difference that a threshold K_{OW} of approximately 2,000 was observed. Again dimethoate was an exception. For multiple DW washes and additional bailing, results were almost identical to those of the DW wash, except that the range of the exponential relationship was much lower. For all three wash treatments the exponential coefficient was very nearly the same (0.000041, 0.0000309, and 0.0000309 respectively), indicating that the relationship between adsorbed concentrations of contaminant and K_{OW} did not change

table 4. Summary of data and analyte properties used for evaluation of effectiveness of bailer decontamination procedures. Values are calculated using the mean of two replicates for low concentration (L) and high concentration (H) initial spike treatments.

Analyte	Initial Spike Concentration Index / [$\mu\text{g/L}$]	K_{ow}	S (water solubility) [mg/L]	C/C ₀ x 100 After Treatment		
				1 DW	> 6 DW	> 6 DW + Bail
diclofop-m	L / 5	37757 ^e	3	0.73	0.40	0
diclofop-m	H / 20	37757	3	1.07	0.50	0.10
methyl parathion	L / 2	1288.2 ^a	60	0.13	0	0
methyl parathion	H / 80	1288.2	60	0	0	0
trifluralin	L / 5	48978 ^a	0.3	2.53	0.50	0.20
trifluralin	H / 50	48978	0.3	1.60	0.80	0.10
MCPA	L / 11	117.5 ^a	825	0	0	0
MCPA	H / 40	117.5	825	0	0	0
dimethoate	L / .2	5.06 ^b	21,000	0	0	0
dimethoate	H / .8	5.06	21,000	4.15	0.30	0
bromoxynil	L / .5	100.0 ^c	130	0	0	0
bromoxynil	H / 50	100.0	130	0	0	0
propicanizole	L / 5	891.3 ^d	110	0	0	0
propicanizole	H / 50	891.3	110	0.49	0	0

a USEPA (1989)

b [Jellinek, Schwartz, and Connolly Inc., Washington D.C.]

c Weed Sci. Soc. Am. (1989)

d Cieba Geigy

e Hoechst Roussel Agrivet

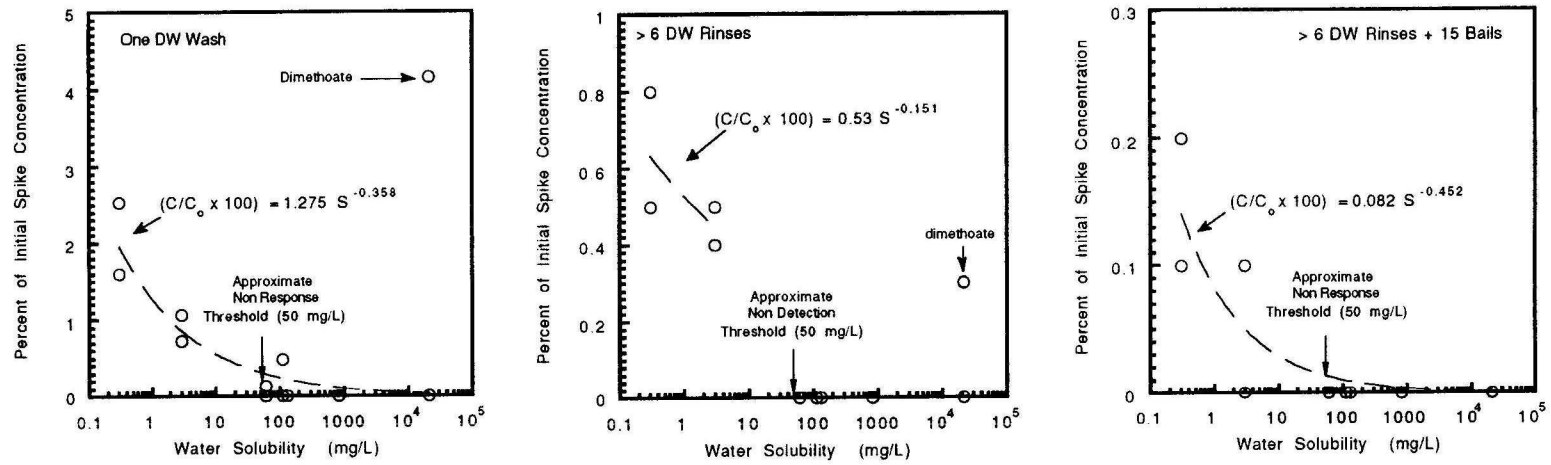


figure 7. Effect of analyte water solubility on rinsate concentration following cleaning treatments.

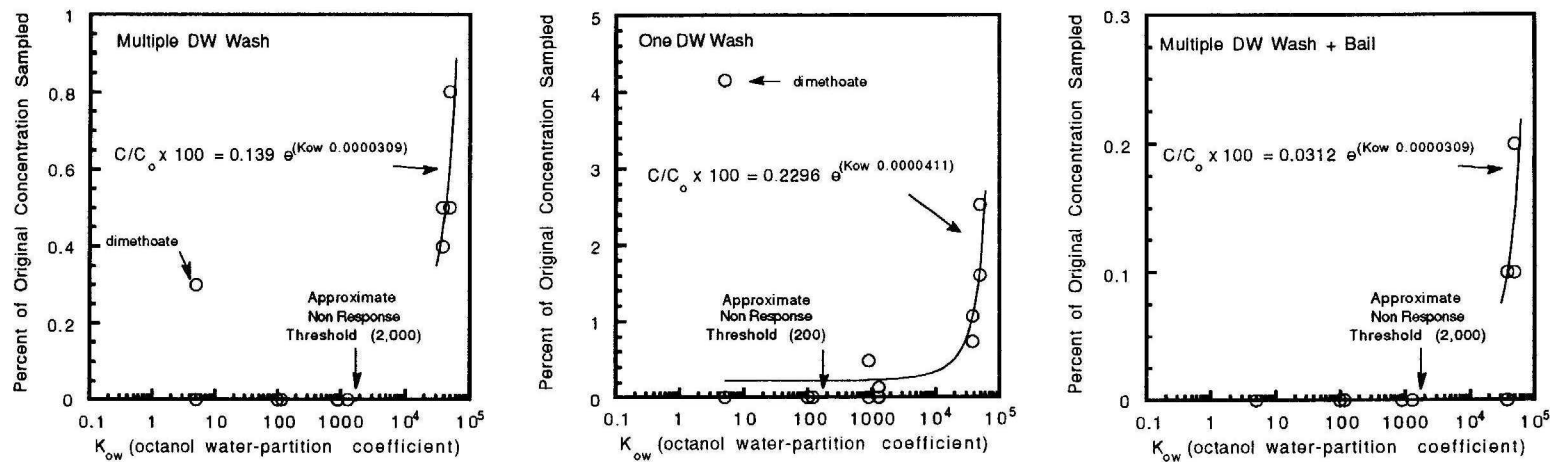


figure 8. Effect of analyte octanol/water partition coefficients on rinsate concentration following cleaning treatments.

with decreasing initial adsorbed contaminant concentrations in successive cleaning operations.

According to these results, many of the phenoxy herbicides (including bromoxynil and MCPA) would be expected to have low adsorption on PVC after brief contact. These results do not seem to agree with the results of Miller et al. (1990) who observed what appeared to be adsorptive loss on PVC in field sampling for pesticides. However, there are many differences between the experiments that might explain this. This experiment involves very short contact times, which may be quite different from the longer apparent times (hours to one day) of Miller et al. Also, other experimental factors could be involved, such as their use of dense polyethylene containers for storage. Further work is necessary to better explain the apparent discrepancies between the results of our findings and those of Miller et al. (1990).

CONCLUSIONS

Results of field tests of bailer cleaning procedures using DW and well bailing alone indicate that bromoxynil, MCPA, methyl parathion, and propiconazole were all adequately cleaned from a PVC bailer by multiple DW washes alone. No trace detections, represented by analytical detection levels below probabilities required for ND-MDL, were noted by chemists for these analytes. Diclofop-m, trifluralin, and dimethoate were all indicated to have been cleaned to levels below ND-MDL after multiple DW washes and 15 bails in a sample well. However, possible trace level residual contaminants (below ND-MDL) were noted for diclofop-m and trifluralin after multiple DW rinses and additional well bailing, indicating less certainty of adequate decontamination. Risk is noted especially for cases where experimental objectives or laboratory precision levels involve very low MDL thresholds. However, even on analytes indicating higher cross contamination risk, decontamination using DW alone was substantial. All contaminants and treatments except dimethoate were indicated to have decontamination efficiencies of 98% or better (based on measured spike concentrations) resulting from one DW wash. Following multiple DW

washes decontamination efficiencies of all contaminants and treatments (including dimethoate) exceeded 99%.

Decontamination efficiencies using DW alone appeared to be related to contaminant solubility and also to the octanol/water partition coefficient. One thorough DW rinse appeared to be sufficient to decontaminate the bailer following brief holding and decanting of contaminants having a solubility of approximately 500 mg/L or more. Multiple DW rinses appeared to be sufficient to thoroughly decontaminate a bailer following holding and decanting of contaminants having a solubility of approximately 10 mg/L or more. Dimethoate was an exception. However, even dimethoate was found to be adequately removed following an additional substantial bailing regime.

Contaminants having a K_{OW} less than 200 seemed to be effectively cleaned by one DW rinse, while contaminants having a K_{OW} less than 2,000 appeared to be effectively cleaned by multiple DW rinses. For larger K_{OW} values, an approximate exponential relationship was observed for contaminants released after washing vs. K_{OW} . A consistent exponential coefficient for all three wash treatments indicated that the relationship between adsorbed materials released after successive wash treatments and K_{OW} did not change with change in initial concentration of contaminant on the PVC surface.

For the brief period of holding in the bailer, a change in analyte concentration due to interaction with PVC was not indicated. There were differences between bailer and spike samples for most sites. However, they appeared to be of a more random character, and were not biased in a decreasing direction that would have indicated adsorption. Also, while some replicates indicated lesser or absent detections, they were not repeated in a consistent manner by other replicates. The use of a PVC well casing or bailer for sampling pesticides used in this experiment and under conditions simulated by this experiment (short contact times) does not appear to cause a significant problems. It does appear, however, that variability of detection would warrant replication of samples for adequate certainty of detection and quantitative assessment .

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