

## Chapter 2

# Methods

### 2.1 Injection/Extraction Possibilities

Push-pull tests can be conducted using any facility or device that makes it possible to inject and extract pore fluids from the formation (Fig. 1.2). Thus, tests may be conducted in open boreholes, screened intervals of conventional monitoring wells, sampling ports of multi-level monitoring wells, drive-points wells, piezometers, or through drive points inserted into the sidewalls of an open excavation. Tests may be conducted above or below the water table, at any depth, and in any type of geologic formation. Tests may be conducted in terrestrial subsurface environments or in saturated sediments that lie beneath lakes, rivers, estuaries, the sea floor, etc. Push-pull tests are most suitable for tests conducted in porous media where flow is laminar but push-pull tests have also been conducted in deep lakes and other surface water bodies where weak turbulent mixing limits dilution losses of injected test solutions. Small-scale push-pull tests have been successfully conducted using the simplest equipment, such as plastic syringes injecting test solutions through “well screens” formed of syringe needles manually inserted into saturated or submerged sediments.

Test locations are typically selected to meet test objectives but it is common and usually desirable to use existing wells, etc. as this reduces the costs associated with well installation, pre-test monitoring, etc.

### 2.2 Volume of Injected Test Solution

The volume of injected test solution is almost always selected to be several times larger than the computed ‘dead volume’ of the injection well to insure that most of the injected test solution penetrates into the formation, rather than simply residing in the well or borehole. The dead volume is calculated from the well or borehole diameter and depth, the length of screen/casing, pump and tubing volume, etc. and

should be increased to reflect the influence of filter/sand packs, formation disturbance due to drilling, etc. as appropriate. The ‘dead volume’ is thus an important factor controlling test duration and cost. Clearly, much larger test solution volumes must be prepared for tests in deep, large-diameter wells, which typically contain larger dead volumes than shallow, small-diameter wells. Larger test solution volumes increases test cost by increasing the size of tank(s), quantities of reagents, and the times required to collect, mix, and inject test solutions. Fortunately, 2 in. and smaller diameter wells are common at most sites and small diameter wells are more commonly being installed to minimize purge volume requirements for routine sampling. However, 4 in. diameter and larger wells are still common, especially at sites where they were installed for active pumping (pump-and-treat remediation, municipal or domestic water production, etc.). Also, at some sites computed volumes for even small diameter wells can be very large if depths are greater than ~100 m. When computed well dead volumes are deemed excessive they may sometimes be reduced through the use of ‘straddle packers’ or similar systems that isolate a portion of the well screen for testing (Fig. 1.2). These are installed in the well to the desired depth and then inflated (or otherwise activated) from the surface using e.g., compressed air. When inflated, the packers prevent vertical movement of water across the packers within the casing, thus reducing the dead volume to the volume of water within the packed interval and the tubing necessary to carry fluids to/from the surface. Straddle packers may also be used as one option when the goal is to conduct a test at a specific depth within a formation. It should be noted that although straddle packers isolate the portion of the well screen through which fluids enter and exit the well, flow to/from a packed interval is not strictly horizontal, especially if sand packs or disturbed zones created by well installation increase the vertical permeability of the formation near the well. Other options for conducting push-pull tests at specific depths include the use of wells/drivepoints, etc. installed at different depths, and the use of dedicated multi-level monitoring wells (Fig. 1.2).

The main factor controlling selection of the test solution injection volume is the desired formation volume to be interrogated during the test. This ‘representative elementary volume’ (REV) should be selected to insure that test results are relevant for the purposes of the investigation. The selection of a suitable REV is ultimately subjective but in general incorporates all relevant site knowledge regarding geology, formation properties, fluid flow patterns, geochemistry, microbiology, etc. As a rough guide, an REV of ~1 m<sup>3</sup> is usually sufficient to capture most important biogeochemical processes occurring in the vicinity of a well. However, much larger and much smaller REV’s have been selected in previous studies (see papers cited in Chapter 3) and the selection is necessarily site and problem specific.

The total volume of the interrogated zone (solids plus pores) can be estimated using:

$$\text{Sample volume} = \frac{\text{Injected volume of test solution} - \text{“dead volume”}}{\text{Formation effective porosity}} \quad (2.1)$$

Equation 2.1 can be modified to account for the volume of annular space between the well casing and borehole wall, the presence of sand packs/filters in the annular space, etc. It should be recognized that the exact three-dimensional shape of the interrogated zone is never known due to heterogeneity in the formation's porosity, permeability, etc., which causes the test solution to penetrate into the formation irregularly, varying with depth and distance from the well. The shape of the interrogated zone will also be strongly influenced by layering, the presence of preferential flow paths (e.g., fractures), density differences between injected test solutions and ambient pore fluids, and by the amounts and kinds of disturbances created by borehole construction and well installation. In practice, the dead volume is first calculated for the test well and then the injected volume of test solution is adjusted to obtain the desired formation volume (subject to the uncertainty in effective porosity). Except for the minimum volume imposed by the dead volume, the injected test solution volume can be increased to achieve any desirable sample volume. Tests have been conducted to interrogate sample volumes of up to  $\sim 100,000 \text{ m}^3$ . However, in most cases, acceptable results can be achieved with sample volumes of 200–1,000 L, which require injection volumes of  $\sim 50$ –500 L, depending on the effective porosity of the formation. Logistical considerations also usually play a large role in selected test solution volumes (Fig. 2.1). The size of available tanks to store and mix test solutions, the weight of tanks and water, the ability to collect sufficient groundwater to fill the tanks, the costs of required chemicals such as tracers, buffers, and dissolved gases, regulatory limits on injection volumes, time required to inject large test solution volumes, and storage or disposal of extracted water during sampling or pumping, are a few of the factors that typically restrict test solution injection volumes to a few 100 L.

A rough estimate of the distance from the well that the test solution penetrates can be computed from the injected test solution volume by assuming that the penetrated portion of the aquifer is cylindrical so that:

$$r_{\max} = \sqrt{\frac{V}{\pi h}} \quad (2.2)$$

where  $V$  is the sample volume computed from Eq. 2.1, and  $h$  is the saturated thickness.

This equation is somewhat useful in providing a rough estimate for the relative volumes of test solution required to penetrate specified distances from the test well but cannot provide an accurate estimate because it ignores the effects on fluid flow of dispersion, diffusion, heterogeneity in formation hydraulic properties, fluctuating water levels, which change saturated thickness, etc. One way to increase the penetration distance without increasing the volume of injected test solution is to reduce the “dead volume” e.g., by injecting test solutions through only a portion of the well screen or borehole wall using a pair of straddle packers as discussed above. This approach is particularly desirable in large-diameter, deep wells. Equations 2.1 and 2.2 clearly show the logistical advantages of using small diameter wells for



**Fig. 2.1** Field push-pull test photographs showing various methods used to prepare and inject test solutions. Clockwise from *upper left*: separately prepared tests solutions in 50 L plastic carboys being combined and injected into a well using a peristaltic pump; 500 L test solution prepared in plastic tank; 240,000 L test solution being transferred from tanker truck to large plastic tank prior to injection; test solution in 200 L plastic drum being injected into monitoring well using a siphon; 50 L test solution in plastic carboy being injected into monitoring well by gravity drainage

push-pull testing; smaller diameter wells have smaller “dead volumes” (all other factors being equal) and larger sample volumes and penetration distances can be obtained in a small diameter well using a given test solution injection volume compared to a large diameter well.

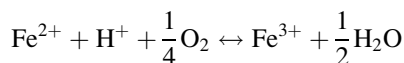
Another factor in selecting the injection volume is the anticipated dilution rate. After injection, the test solution will be diluted with ambient pore fluids as the test solution flows away from the injection location. Concentrations of injected tracers will decrease and eventually reach nondetectable or background levels. The ability of a push-pull test to provide useful information is determined to a large degree by the relationships between injected test solution volume, the dilution rate, and the time required for the test solution to remain in the formation to provide useful results. For example, if the goal is to measure the rate of transformation of an injected reactive tracer, it will be necessary to keep the injected test solution in the vicinity of the well long enough to allow the reaction progress to be observed. This is most easily achieved if reaction rates are large and dilution rates are small. In that case, the injected test solution volume can be selected solely to meet other scientific

or logistic objectives. However, if reaction rates are anticipated to be small and/or dilution rates are anticipated to be large, it is possible that the injected test solution will migrate away from the vicinity of the well too quickly to provide any useful information. In this case, the injection volume can be increased beyond that determined by other factors in an attempt to compensate for the higher anticipated dilution rate. Simple calculations with Darcy's Law, effective porosity, and assuming a cylindrical zone of influence are usually adequate to estimate a suitable injection volume. Of course these calculations are only approximate as the dilution and reaction rates are not known a priori (otherwise there would be no point in conducting the test!). However, even approximate calculations based on crude rate estimates are usually sufficient to select a test solution volume that insures a successful test. Nevertheless, it is usually desirable to conduct a simple test with a nonreactive tracer to estimate the dilution rate prior to injecting expensive or difficult-to-prepare test solutions or performing time-consuming or expensive sampling and analyses. In many cases, simple injections of tap water followed by periodic measurements of electrical conductivity or some similar field parameter are sufficient to determine how long injected test solutions will reside in the formation near the test well. For example, if tap water is injected, the changing chemical composition of the test solution may be indicated by a changing electrical conductivity that will vary between the injected tap water and ambient groundwater at a rate that is roughly proportional to the dilution rate. Of course for this type of test to succeed requires a diagnostic chemical signature between injected and ambient porefluids.

The desired test solution volume is also usually modified to accommodate various site-specific logistical factors. For example, containers available for preparing test solutions may have a fixed size (e.g., 200 L drums are common at many contaminated sites and farm supply stores sell plastic tanks in incremental sizes up to ~5,000 L) or makeup water may have to be hauled in trucks with fixed weight carrying capacity. Costs of tracers, compressed gases, etc. also increase as the test solution volume increases and these costs must also be included in the decision making process. Another important cost factor is the time required to inject the test solution, which is ultimately limited by the formation permeability and by the diameter and length of the screened interval. While injection rates of ~1 L/min are common, the possible range is extremely wide, from a few mL/min to tens of L/min. Obviously, injecting large test solution volumes in small diameter wells installed in low permeability materials may require many days and can be the rate-limiting factor in determining overall test duration and cost. Moreover, push-pull tests used to determine pore water velocities, mass transfer coefficients and sorption characteristics may require the extraction of between two and five times the volume of injected test solutions and this can add considerably to the time required to complete these types of tests. However, with experience, a balance of all of these factors can be readily achieved to meet test objectives.

## 2.3 Test Solution Composition

The type of test is used to determine the composition of the injected test solution. The first decision is to select a suitable liquid or gas to which various chemical amendments will be added. In saturated zone tests, test solutions are typically prepared from site groundwater in an attempt to insure that test results represent in situ conditions as closely as possible. Using site groundwater preserves the concentrations of major and minor ions, dissolved gases and other volatile constituents that may play a role in the specific chemical or biological reactions or processes under investigation. For example, site groundwater could be extracted from each test well, modified to the minimum extent possible by adding only necessary tracers, etc. and then injected into the same well. The knowledge and experience of the investigator is used to select those features of the site groundwater that should be preserved during test solution preparation and these will influence the details of above-ground operations. For example, test solutions may be collected in inflatable bladders rather than tanks to avoid the loss of volatile components and exposure to atmospheric oxygen or in insulated containers to avoid temperature changes while test solutions are manipulated above-ground. Of course all of these provisions will create logistical difficulties and increase the time and cost of testing. It should be mentioned that the generally high reactivity of subsurface sediments will quickly modify some attributes (e.g., pH) of injected test solutions and that the contribution of trace reactive components in site groundwater are typically overshadowed by the much higher concentrations of reactive species associated with mineral surfaces, immobile water, etc. present in the aquifer. For this reason, the need to take extreme care to preserve all features of site groundwater during test solution preparation should be critically evaluated. As a simple example, many contaminated aquifers may contain large quantities of reduced iron (mmol to mol  $\text{Fe}^{2+}$ /kg of sediment) produced by microbial iron reduction. This  $\text{Fe}^{2+}$  will rapidly react with any trace dissolved  $\text{O}_2$  remaining in injected test solutions, removing  $\text{O}_2$  from solution:



Similar reactions may result in the precipitation of other reduced metals, sulfides, etc. Thus, in anaerobic environments taking extreme care in avoiding the introduction of trace amounts of  $\text{O}_2$  ( $\sim\mu\text{mol/L}$ ) during above-ground test solution preparation (which can be very difficult) may not be warranted. Also, most chemical reactions of interest are generally insensitive to changing concentrations in major inorganic ions, etc. so that attempting to create a synthetic groundwater with the exact composition of ambient groundwater may not be worth the cost or effort.

In many cases, test solutions prepared from distilled water, tap water, or synthetic groundwater are used in place of site groundwater (typically to avoid some of the logistical issues identified above or for regulatory reasons) where it is believed

that test results will be largely unaffected by the exact chemical composition of the injected test solution. Some examples are nonreactive tracer tests performed to characterized ambient pore fluid velocities, effective porosity, dispersivity, and mass transfer coefficients. Using these types of makeup waters can greatly reduce the time and cost of field testing; test solutions prepared from tap water or other readily available bulk water sources have been widely and successfully used for many types of tests. Similar considerations pertain when selecting gases to prepare test solutions for vadose zone tests; the trace impurities present in lower quality and lower cost readily available compressed gases typically have no effect on test results compared to using higher-purity, special order gases.

The number, type, and concentration of tracers included in the injected test solution depend on the purpose of the test. Tests to determine pore fluid velocity, formation dispersivity, mass transfer coefficients, etc. are typically conducted using only nonreactive tracers, while tests to determine reaction rates are conducted with one or more additional reactive tracers as needed to interrogate the targeted process.

Many nonreactive tracers are available and include inorganic anions ( $\text{Br}^-$ ,  $\text{Cl}^-$ , etc.), organic anions (chlorinated or fluorinated benzoic acids), dissolved gases ( $\text{SF}_6$ , He, Ar, Ne), and many other possibilities. Selecting a nonreactive tracer depends on a number of factors including the chemical composition of ambient pore fluids, the availability and cost of suitable analytical methods, tracer costs, and the objectives of the test. The nonreactive tracer should not be present at high concentrations in the ambient pore fluid as this will complicate the calculation of dilution-adjusted concentrations. However, if nonreactive tracer concentrations in ambient groundwater is high, it may be possible to inject test solutions with no nonreactive tracers and still calculate dilution-adjusted concentrations (e.g., tests conducted in salty groundwater, seawater, or brines). Thus,  $\text{Cl}^-$  and  $\text{Br}^-$  are generally suitable choices for nonreactive tracers for use in tests conducted in low ionic strength groundwaters, which typically have low  $\text{Cl}^-$  and  $\text{Br}^-$  concentrations, but may not be suitable for tests conducted in groundwater containing higher concentration of these ions or perhaps other ions that create analytical interferences. For example, the use of  $\text{Cl}^-$  as a nonreactive tracer is problematic where the subsurface is impacted by seawater or brine (e.g., in coastal locations or certain depositional environments), which typically have large  $\text{Cl}^-$  concentrations. Similarly the presence of high  $\text{Cl}^-$  concentrations in ambient porefluids may complicate accurate quantification of  $\text{Br}^-$  added to injected test solutions due to analytical interferences (e.g., by ion chromatography). It is always desirable to verify analytical methodology in the laboratory (e.g., by spiking nonreactive tracer into a sample of ambient porefluid) prior to field testing. Inorganic tracers are typically analyzed by ion specific electrodes, ion chromatography, or inductively-coupled plasma mass spectrometry. Organic tracers are typically analyzed by flourometry, spectroscopy, ion chromatography, gas chromatography, or liquid chromatography, while gas tracers are typically analyzed by gas chromatography.

The concentration of nonreactive tracer(s) used should be given careful consideration. As a preliminary guide, many tests utilize injected tracer concentrations that are approximately 100 times larger than the analytical detection limit. For example,

if  $\text{Br}^-$  analysis by ion chromatography has a detection limit of  $\sim 1$  mg/L then a suitable  $\text{Br}^-$  concentration for the injected test solution would be  $\sim 100$  mg/L. This allows for the accurate determination of tracer concentration as injected test solutions are diluted by ambient pore fluids during the test. When the analytical detection limit is reached, samples collected from the well will consist of  $\sim 1$  % injected test solution and  $\sim 99$  % site groundwater. When dilution rates are anticipated to be large (i.e. ambient porefluid velocity is anticipated to be large) it may be tempting to increase tracer concentration and some tests have been conducted with very high tracer concentrations (up to 250,000 mg/L!). However, experience has shown that the use of such high tracer concentrations is almost always counter-productive and results in *increased* dilution losses due to buoyancy induced vertical sinking of injected test solutions caused by density differences between the test solution and the ambient pore fluid. It also may be necessary to consider the effects of density differences on the degree of mixing (or lack of mixing) that occurs between injected test solutions and pore fluids within the well casing and screen. The overall result is larger apparent dilution losses of injected test solution. High concentration and therefore high density test solutions will also sink to the bottom of wells and boreholes and cause injected test solutions to preferentially penetrate deeper portions of the formation. The latter effect can be partially ameliorated by mixing the contents of the well casing during test solution injection but density driven flow will still occur in the formation whenever there is a significant density difference between injected test solutions and ambient pore fluids.

It should also be noted that the addition of high concentrations of nonreactive tracers can sometimes have additional unintended consequences. For example, the addition of high concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc. (present in salts used as a source of  $\text{Cl}^-$ ,  $\text{Br}^-$ , etc.) to the subsurface can alter the charge balance on clays and other mineral surfaces resulting in decreased porosity and permeability of the formation or in the release of ions from mineral surfaces (e.g., heavy metals, radionuclides, some organics) by cation exchange and/or mass action. High salt concentrations may also decrease the solubility of other test solution components in sometimes complex and unpredictable ways, making it difficult to maintain the desired overall composition. For these reasons, the consequences of using test solution tracer concentrations greater than a few hundred mg/L should be critically evaluated and rigorously tested in the laboratory prior to field implementation.

The choice of reactive tracer(s) is also a critically important part of push-pull test design and these are determined by the purpose of the test. As the Chapter 3 and Examples sections describe, tests have been conducted to examine the reactivity of a wide variety of such tracers including dissolved gases (e.g. oxygen and methane), organic contaminants (e.g. chlorinated solvents such as trichloroethene and petroleum hydrocarbons such as toluene), inorganic contaminants (e.g. heavy metals such as chromium and radionuclides such as uranium and technetium), and many others. In addition to the considerations listed above for nonreactive tracers, selecting the type and concentration of reactive tracers may require a number of additional factors. For example, the reactivity of many of these tracers will depend on concentration and the presence of other components in solution. For example,

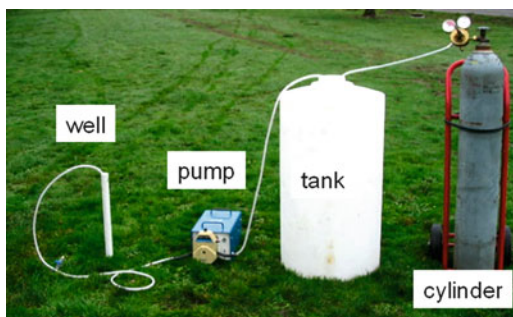


the reductive dechlorination of a chlorinated solvent typically depends on the concentration of both the electron acceptor and electron donor (e.g. trichloroethene and hydrogen) as well as other factors and these must be considered in designing test solutions aimed at quantifying rates of reductive dechlorination. Similarly,  $H^+$  and  $HCO_3^-$  participate in many chemical and biological reactions and modifying or maintaining ambient concentrations of these ions may be desirable. The Examples should give preliminary guidance and it is also desirable to review protocols used in laboratory experiments to identify the specific combination of nonreactive tracers and other test solution components required to interrogate a specific reaction.

## 2.4 Test Solution Preparation

Test solution preparation is largely a matter of collecting a sufficient quantity of makeup fluid and modifying it in various ways to obtain the desired composition before it is injected into the subsurface. For aqueous test solutions, this usually involves first filling a glass or plastic container with makeup water and then mixing in various chemical or other amendments. It is important to classify the desired test solution components by their physical form (solid, liquid, gas) and chemical properties (solubility, volatility, etc.) in order to select an appropriate container and method of mixing. For example, anionic tracers like  $Br^-$  and  $Cl^-$  are added as salts (e.g., NaCl, KBr) and these are highly water soluble, not expected to sorb to glass or plastic, and are nonvolatile. Thus, adding these tracers to aqueous test solutions involves simply adding the desired amount of the appropriate salt (NaBr, NaCl, etc.) to a known volume of water in any suitable container and mixing by any convenient method until a constant composition is obtained. However, even in this simple case, a number of additional considerations may arise. For example, if test solutions are prepared from site groundwater it should be recognized that the addition of salts and the agitation of mixing may cause undesirable physical/chemical affects. For example, the addition of salts may decrease the solubility of other aqueous species and may lead to the precipitation of various mineral phases. Also exposure of the makeup water to the atmosphere and the agitation required for mixing may increase the dissolved oxygen content of the test solution and lead to the oxidation of reduced species (e.g.  $HS^-$ ,  $Fe^{2+}$ ) and the precipitation of oxides, sulfides, etc.. Mixing may also lead to the loss of volatile components and these also may have undesired consequences. For example, loss of dissolved  $CO_2$  may lead to an increase in pH, decrease in  $HCO_3^-$ , decreased solubility of various metals, precipitation of various mineral phases, etc. Temperature and pressure changes during test solution preparation may sometimes have similar undesirable or unanticipated effects (e.g., degassing caused by depressurization when ambient groundwater is brought to the surface). The combined effects of all of these processes are difficult to predict with complete confidence. Nevertheless, in the vast majority of tests it is a relatively simple matter to keep the magnitude of these effects small and if a particular effect is deemed undesirable for a particular type of test, field

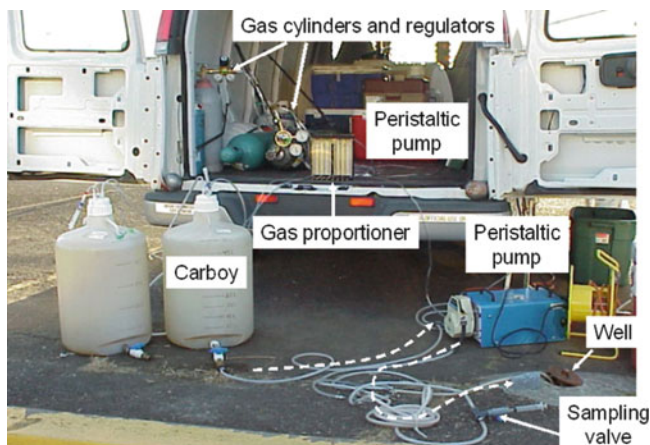
**Fig. 2.2** Example simple setup for mixing test solutions in plastic tank using compressed gas supplied by the cylinder to porous stones placed in the bottom of the tank containing the test solution. After mixing, the test solution is injected into the well using the peristaltic pump



procedures may be easily modified to eliminate that effect and produce a test solution with the desired composition as discussed below.

The dissolved gas composition of an aqueous test solution can be controlled in several ways. For example, if the goal is to maintain the dissolved gas composition of ambient groundwater during test solution collection and preparation, site groundwater can be collected in inflatable, gas-impermeable bags or bladders to prevent the loss of volatile groundwater components or the introduction of atmospheric gases. If instead the goal is to change the dissolved gas composition in a prescribed manner, this can often be accomplished by bubbling compressed gas mixtures through the makeup water. One effective way for doing this is to place several porous stones (e.g., of the type used in home aquariums) in the bottom of the container and connecting these to compressed gas cylinders or other sources of compressed gases by plastic tubing (Fig. 2.2). For example, a small pump or compressor can be used to deliver air to the stones and bubble air through the makeup water, while compressed gas cylinders can be used to deliver  $O_2$ ,  $CO_2$ ,  $SF_6$ ,  $H_2$ , etc. Gas bubbling has proven to be an effective method for mixing test solution components and the number of stones and the gas pressure can be easily increased to mix test solutions of any size. Compressed gas is often more convenient than mechanical mixers because a single standard compressed gas cylinder can be used to simultaneously mix many large tanks of water by simply extending/splitting gas delivery lines as needed. Compressed gas mixing requires no electrical power and many commercial vendors for a wide variety of compressed gases are available so that obtaining gas cylinders is usually not difficult, even at remote sites. Using compressed gas allows test solutions to be mixed unattended for many hours or days if necessary, which can substantially increase overall test productivity. A common approach is to mix solutions overnight prior to the start of test solution injection and to continue bubbling during injection.

Perhaps most importantly, using compressed gases to mix aqueous test solutions makes it possible to control certain aspects of the chemical composition of the test solution. This is done by specifying the flow rate(s) or partial pressure(s) of the supply gases to achieve the desired dissolved gas concentrations. For example, bubbling with compressed air or oxygen can be used to add dissolved oxygen to test solutions; similarly bubbling with compressed  $N_2$  or Ar can be used to remove



**Fig. 2.3** Test solution prepared by bubbling three separate gases simultaneously. Gas flow rates from the cylinders to the porous stones in the carboy are controlled using the gas proportioner, which contains a separate float-type flowmeter and adjustable needle valve for each supply gas. Dissolved gas concentrations are computed from gas properties, flow rates, and temperature. After mixing, the test solution is injected into the well using the peristaltic pump; samples are collected to verify concentrations of all components

dissolved oxygen from test solutions. Specified dissolved oxygen concentrations between zero and saturation can be easily achieved by bubbling with a prepared gas mixture with given partial pressures of  $O_2$  or by bubbling two separate gas streams ( $O_2$  and another gas, e.g.,  $N_2$ ) at proportional flowrates through the test solution (Fig. 2.3). Specified concentrations of other dissolved gases (He, Ne,  $SF_6$ ,  $H_2$ ,  $CH_4$ ,  $C_2H_2$ ,  $CO_2$ , etc.) can also be achieved by bubbling mixtures of those gases through the test solution. Estimates for the conditions needed to achieve the desired dissolved gas composition can be obtained from tables of gas solubility, Henry's Law constants, etc. for a given partial pressure and temperature; but these estimates should be confirmed prior to field deployment. It should be mentioned that unusual gas mixtures may be easily and inexpensively prepared by first combining various partial pressures of pure gases in a suitable empty cylinder using a transfer device built from high pressure tubing and appropriate regulators. Once the gas cylinder containing the mixture is prepared, the gas mixture from that cylinder is bubbled through the test solution as usual to achieve the targeted concentrations of all components.

It is important to recognize that bubbling dissolved gases through the test solution may result in other (perhaps unintended) chemical composition changes. For example, if test solutions are prepared from site groundwater, the concentration of volatile contaminants and dissolved gases will be reduced (unless these are present in the compressed gases bubbled through the test solution). This may be desirable in some situations, (e.g., to remove dissolved oxygen), but not in others (e.g., if the reactivity of volatile components of ambient groundwater will be studied during the test). It is important to note that loss of dissolved  $CO_2$  may change the pH and other

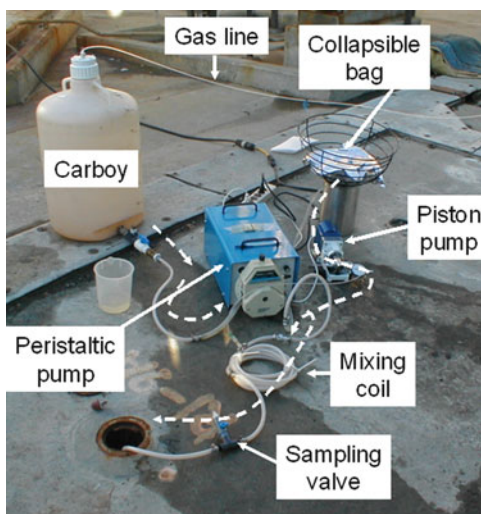
characteristics of the test solution (e.g., pH affects the solubility of many dissolved metals). For this reason, it is often desirable to include CO<sub>2</sub> in the gas mixture (e.g., an anoxic test solution might be prepared by bubbling a gas mixture of 80 % N<sub>2</sub> and 20 % CO<sub>2</sub>) and to monitor pH during mixing and injection.

Adding the various chemical amendments followed by mixing with compressed gases is a convenient method for preparing aqueous test solutions in many cases. However, this approach may not be suitable if some components of the test solution are toxic, expensive, or can only be purchased in liquid form. For example, while it may be desirable to prepare aqueous test solutions containing known concentrations of a volatile organic solvent it may not be practical to bubble solvent vapors through the test solution because of costs and difficulties in preparing and pressuring a suitable gas phase, capturing and treating potentially toxic gas streams leaving the tank, and achieving a constant composition. Also, to achieve certain chemical compositions it may be necessary to bubble potentially flammable or explosive gas mixtures through the aqueous test solution (hydrogen, acetylene, oxygen, methane). Moreover, some specialty gases are very expensive and it may not be cost effective to bubble sufficient quantities of gas through the test solution to achieve targeted concentrations.

In these cases, alternate approaches may be used to prepare aqueous test solutions with specified concentrations of dissolved gas or other volatile components. One approach is to use a coil of gas permeable tubing immersed in the test solution. The tubing is connected to a compressed gas cylinder. When pressurized, gas is transferred to the test solution by diffusion through the tubing walls without bubbling. A related approach is to add prepared solid phases (e.g., activated carbon) or nonaqueous phase liquids (e.g., mineral oil) containing the targeted compound directly to the makeup water. In this case, gas is transferred by diffusion from the interior of the solid or nonaqueous phase liquid to the makeup water. These approaches can be effective and extremely convenient but they usually require preliminary laboratory testing to insure that desired uniform concentrations are achieved (e.g., diffusion is a rather slow process and diffusion rates will depend on temperature, material properties, and a number of geometrical factors; in any case, some form of mechanical mixing may be required to achieve uniform concentrations within a large volume).

An alternate approach for formulating aqueous test solutions with volatile components that has many practical advantages is to prepare small volumes (1–10 L) of concentrated aqueous solutions of these materials in collapsible bags (Fig. 2.4). These bags are commercially available, are constructed of various inert and gas-impermeable materials (e.g., Teflon), and are available in a wide variety of sizes. The bag is first filled completely with water leaving no headspace. Then a syringe is used to inject known quantities of gases or other substances into the bag, which can then be mixed by hand (e.g., by “gentle scrunching”). For example, an aqueous test solution containing a known concentration of dissolved ethene could be prepared by injecting the required volume of ethene gas (at a specified pressure and temperature) into a collapsible bag filled with site groundwater using a gas-tight syringe. Additional test solution components can be sequentially added as needed to

**Fig. 2.4** Nonvolatile test solution components are prepared in the plastic carboy; volatile test solution components are prepared in the collapsible Teflon bag. The two solutions are combined during injection to obtain the desired overall composition. The “mixing coil” is used to insure complete blending of the two solutions before they are injected. Test solution composition is verified by analyzing samples collected from the sampling valve



achieve the desired overall test solution composition. As the test solution is pumped from the bag during injection, it collapses, maintaining a zero head space condition within the bag and thus preventing losses of volatile test solution components. Other advantages of this approach are that (1) only small quantities of gases or other solutes are required, and (2) the entire system is closed, minimizing losses of volatiles to the atmosphere, chemical exposure of field personnel, etc.

It is sometimes desirable to combine various approaches for preparing aqueous test solutions. For example, nonvolatile test solution components can be prepared in a tank open to the atmosphere and mixed with compressed air or other gases, while volatile test solution components can be prepared as aqueous solutions in small collapsible bags as described above. The two solutions, prepared separately, can be combined (e.g., using two pumps or a single pump with two pump heads) during injection to achieve a test solution with the desired overall composition (Fig. 2.4). By calibrating the pumps at the correct flow rates, virtually any desired concentrations of volatile and nonvolatile test solution components can be achieved. This approach also allows for the possibility of changing test solution composition in a defined way during injection. For example, the concentration of one component can be varied by varying the flow rate of the pump used to transfer the solution containing that component.

Gaseous test solutions used in vadose zone tests can also be prepared to any desired composition. In one approach, the various gases that makeup the test solution are stored in separate compressed gas cylinders, and mass flow controllers are used to combine the separate gas streams at known rates to obtain the desired composition. Alternatively, a customized gas mixture is prepared by transferring portions of each gas to an empty cylinder to achieve a mixture with the desired partial pressure of each gas. Finally, gases can be introduced into collapsible bags as described above, mixed, and then injected using a pump.

In all cases, the composition of aqueous and gaseous test solutions should be confirmed by periodic sampling during the injection phase. The potential difficulties in creating precisely controlled chemical compositions in large aqueous or gaseous volumes cannot be overemphasized. If possible, the procedures to be used to prepare test solutions in the field should first be evaluated with identical equipment, etc. in the laboratory. Particular care should be taken in confirming the ability to produce desired concentrations of highly volatile or low solubility components. During field testing, samples of the test solution should be collected from the early, middle, and late portions of the injection period because several time-variable factors can contribute to unanticipated changes in test solution composition during injection. For example, temperature may change during the day, affecting solubility, vapor pressure, etc., pump calibrations may change as water levels in tanks and wells change, or mass flow controllers may also drift out of calibration as supply gas pressures change.

## 2.5 Test Solution Injection

A number of factors influence the injection method including: the volume and composition of the test solution, the depth and conductivity of the aquifer, well construction details, and a number of logistical issues (number of tests, availability of pumps, power, etc.). Aqueous test solutions may be siphoned or pumped into the well or added manually (“poured”) in aliquots using suitable containers. Siphons are convenient in situations where the injection times are anticipated to be large (large volumes of aqueous test solution or small formation conductivity). However, it can be difficult to control injection rates (because of varying water levels) unless in-line valves and flow meters are used but for most types of tests the exact injection rate is not needed to interpret test data. Pumps of various kinds are widely used to inject aqueous test solutions, and are usually required if precise control of injection rate is required (e.g. in tests designed to estimate regional groundwater velocity). Injection rates for aqueous test solutions can be monitored by volumetrically measuring water levels in the supply tank, weighing collapsible bags using a portable scale, or with inexpensive in-line flow meters. Gaseous test solutions are typically injected using pressure from the compressed gas cylinders and injection rates are controlled by controlling the supply pressure and measured using in-line gas flow meters.

It is important to recognize that injection rates are often limited by formation permeability and well construction details (e.g. well screen length, presence of filter pack) and the condition of the well screen (old wells often have partially clogged screens). When aqueous test solutions are injected into a well, water levels in the well will rise. Depending on the length and location of the screened interval, the thickness of the annular space between formation and well casing, and the presence of filter packs, seals, etc., rising water levels (water tables in unconfined aquifers, piezometric surfaces in confined aquifers) can result in some test solution flowing upward and outward into the vadose zone above the pre-test water level

(or overflowing wells at the land surface in shallow tests). In addition to delivering a portion of the prepared test solution to a part of the formation that may not be the subject of study, some of the test solution injected into the vadose zone will be retained by capillary forces and will not be accessible for subsequent extraction and sampling, thus increasing dilution losses. A similar process can occur with gaseous test solutions. Water levels or gas pressures should be monitored during injection using suitable water level meters or pressure gages. In fact, by measuring flowrates and pressures during test solution injection, it is possible to determine the formation permeability using conventional pumping test theory and analytical methods during a push-pull test with little added effort.

Test solutions usually enter the well through tubing that extends from the surface to a point within the screened interval of the well. If the well screen is long or the well diameter is large, injected test solutions may not completely mix with the “dead volume” of fluid stored within the casing, resulting in varying concentrations of test solution components entering the formation (e.g. lower concentration higher up in the saturated zone). Incomplete mixing above ground or in the well casing is another form of “dispersion” that will contribute to increased dilution losses and “tailing” of concentration profiles, which might be confused with mass-transfer processes such as diffusion controlled sorption. In many situations, this effect is relatively small compared to dilution losses caused by regional flow, formation heterogeneity, buoyancy induced flow, etc., and may not be significant if the volume of injected test solution is much larger than the well “dead volume” (this is another reason why push-pull tests are easier to conduct in small diameter wells). If deemed important, this problem can sometimes be ameliorated by mixing the contents of the well casing during test solution injection (and perhaps during subsequent sampling). One simple way that this can be accomplished is by inserting a weighted porous stone attached to a gas supply line (like those used to mix test solutions with compressed gas) to the bottom of the well, and bubbling the contents of the well casing with a suitable compressed gas. Care in mixing the contents of the well is particularly important for certain types of push-pull tracer tests that assume solute concentrations in fluids leaving and entering the well are uniform across the formation thickness. Another push-pull test variation is to simply bubble gas mixtures in the well with no aqueous solution injection and allow regional flow and diffusion to transfer tracers from the well to the formation. This approach has the advantage that no above-ground storage or preparation of test solutions is required to introduce gaseous tracers into the formation.

Test solutions may be injected across the entire length of an uncased borehole, across the entire length of the screened interval of a well, from the tip of a drive-point, or from a multi-level well screen. In some cases it is desirable to conduct push-pull tests within particular depth intervals in uncased wells or wells with long screened intervals. Straddle packers may be used for this purpose. Straddle packers are lowered to the desired depths and inflated to isolate a portion of the borehole or well casing. The test solution is then injected and extracted from the portion of the well screen between the two packers. Dedicated multilevel wells or multiple closely-spaced wells installed at different depths may also be used for this purpose.

The total volume of test solution injected should be recorded (e.g. by recording falling water levels in the tank(s) used to prepare the test solution) as this provides an estimate of the formation volume interrogated during the test and is useful for computing mass balances. For aqueous test solutions mass balance calculations are performed by integrating measure concentrations and volumes during injection. For gaseous test solutions, these calculations are performed by integrating measured gas flow rates, pressures, and temperatures during injection.

In some cases, test solution injection is immediately followed by injection of a “chaser” solution into the well. The “chaser” typically contains no added tracers. “Chaser” injection insures that all injected test solution is pushed out of the well casing and into the formation. Although this may be required for certain types of tracer tests (i.e. those aimed at determining pore fluid velocities or mass transfer coefficients) it should not be adopted as a general practice since the injected “chaser” will also lead to increased dilution of the injected test solution.

## 2.6 Extraction/Sampling

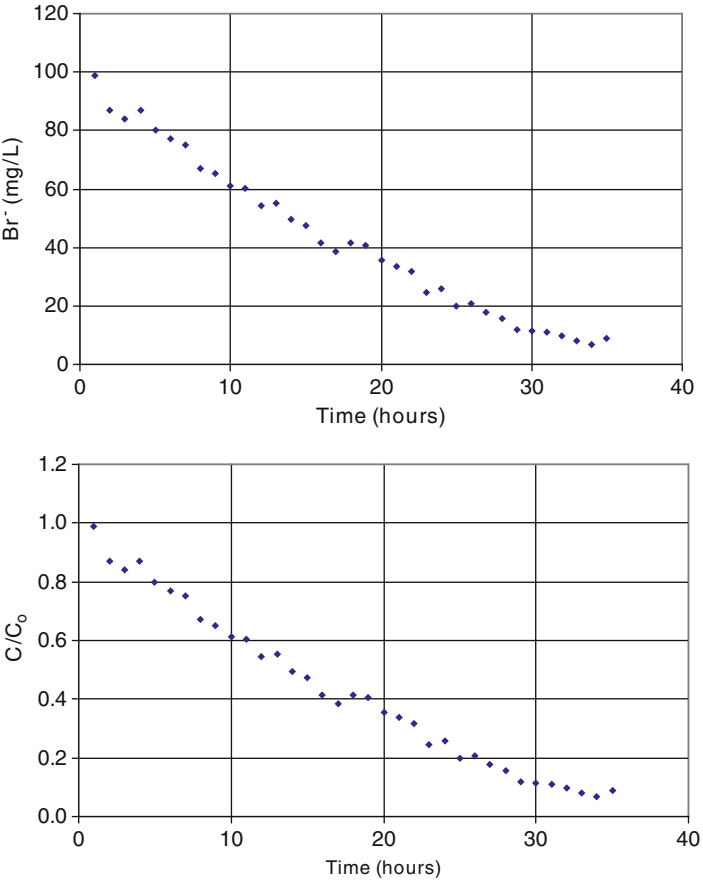
After injection is completed, samples of the test solution/pore fluid mixture are collected in a variety of ways that depend on the purpose of the test. For many types of tests, the test solution is injected and then samples of the test solution/pore fluid mixture are collected as a series of discrete sampling events distributed over a defined period of time. For other types of tests, extraction pumping begins immediately after test solution injection is complete and continues at a constant rate until a pre-determined total volume has been extracted. A “rest phase” with no pumping may be included between the injection and extraction phases (e.g. to allow the injected test solution to drift with regional flow). The overall goal, of course, is to allow the test solution to reside in the formation long enough to detect the targeted process or reaction. Thus, tracer tests designed to measure fluid velocity require that the test solution reside in the formation sufficiently long to be advected downgradient from the well. Similarly, longer residence times may be required for tests aimed at determining diffusion-controlled mass transfer coefficients or small (slow) reaction rates. Of course, sampling frequency could only be optimized if the ambient fluid velocities, reaction rates etc. were known prior to the start of the test! Thus, whenever possible it is desirable to perform sample analyses while the test is in progress so that the need for continued sampling can be evaluated in “real time”. Perhaps the largest uncertainty is in the dilution rate and, in general, samples collected after nonreactive tracer concentrations have fell below background levels will provide any useful information. Thus, at a minimum, it is desirable if nonreactive tracer concentrations be determined after each sampling event. When this is not possible, it is often desirable to sample more frequently and to continue sampling for a longer period of time to insure that that sampling captures the process of interest. Then, the costs of sample analyses can be optimized in the laboratory (e.g., analyzing nonreactive tracer concentrations first, analyzing “every-other” sample, etc.)



## 2.7 Data Analysis

Data analysis begins by preparing concentration profiles (i.e. measured concentration vs. time) for all injected tracers and any products formed in situ and, in general, these are interpreted using the same techniques used to interpret any laboratory experiment, *with one important exception*. The concentration profiles of the reactive tracers and reaction products must first be adjusted for dilution using measured concentrations of the nonreactive tracer(s). A useful analogy is to consider push-pull test data to have come from a “leaky batch reactor”. Each sample collected during the extraction phase of a push-pull test is typically a blend of the injected test solution and the ambient pore fluid (which “leaks” into the test volume), i.e. the injected test solution has been “diluted” by ambient pore fluid and each sample is actually a mixture of the two fluids. For example, Fig. 2.5 shows an example concentration profile for a  $\text{Br}^-$  tracer injected at an initial concentration of 100 mg/L. With time the injected test solution migrates away from the well and the  $\text{Br}^-$  concentration decreases. By plotting the relative concentration,  $C/C_0$ , where  $C$  is a measured  $\text{Br}^-$  concentration and  $C_0$  is the  $\text{Br}^-$  concentration in the injected test solution (Fig. 2.5), it is possible to quantify the extent of dilution that has occurred. Thus, in Fig. 2.5, a sample collected 20 h after injection has a measured  $\text{Br}^-$  concentration of 36 mg/L and a relative concentration of 0.36. The latter is interpreted to mean that this sample consists of a mixture of 36 % injected test solution and 64 % ambient groundwater. As will be shown in the Examples, relative concentrations for injected nonreactive tracers are used to compute *dilution-factors*, which are then applied to measured concentrations of reactive tracers to obtain *dilution-adjusted concentration profiles* for the reactive tracers. Dilution-adjusted concentration profiles are used, for example, to compute reaction rates. Of course, several assumptions and conditions are required when applying dilution factors computed from a nonreactive tracer to a reactive tracer and these will be discussed in the Examples.

A variety of specific methods have been developed to interpret push-pull test data for different applications and these are described in detail in the Examples and the primary literature. It should be noted that several features of the push-pull test contribute to simplify data analysis. For example, push-pull tests are generally less sensitive to aquifer heterogeneity than well-to-well tests because of the flow reversal that occurs between injection and extraction phases. For this reason, concentration profiles obtained from push-pull tests tend to be relatively smooth, with simple monotonic decreases in injected tracer concentrations, etc. Nevertheless, each method of data analysis involves making certain simplifying assumptions and the validity of these should be evaluated for each specific application, as discussed in the Examples.



**Fig. 2.5** Example concentration profile for injected  $\text{Br}^-$  as a nonreactive tracer. The relative concentration,  $C/C_0$ , where  $C$  is a measured  $\text{Br}^-$  concentration in an extraction phase sample and  $C_0$  is the  $\text{Br}^-$  concentration in the injected test solution, serves as a measure of dilution



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