in short-lived bird species the population dynamics are more strongly influenced by the recruitment of new individuals into the population, whereas in long-lived birds the dynamics are more strongly influenced by the survival rates of the adults that are already present in the population. Understanding the association between population dynamics and birth, death, and dispersal rates requires that detailed data be collected from marked individuals. This knowledge is crucial for wildlife managers, as it identifies the key demographic rate that should be targeted to reverse population declines or to prevent population eruptions. The findings of Sæther *et al.* demonstrate that generalizations might exist. The next step will be to attempt to confirm these generalizations with more data sets from a wider range of populations and species.

Sæther *et al.* show that there are predictable differences between the population dynamics of species with different life histories. They present a benchmark study in the relatively new field of comparative population dynamics. However, the enormous potential of this field can only be realized if data sets of sufficient length and quality continue to be collected and analyzed. Achieving this goal will require international collaboration between ecologists and statisticians, as well as the goodwill of researchers who have invested many years of their careers in collecting detailed data. Our ability to make generalizations about population dynamics will facilitate conservation efforts, and so benefit future generations.

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PERSPECTIVES: ENVIRONMENTAL CHEMISTRY

Tracking Hexavalent Cr in Groundwater

David Blowes

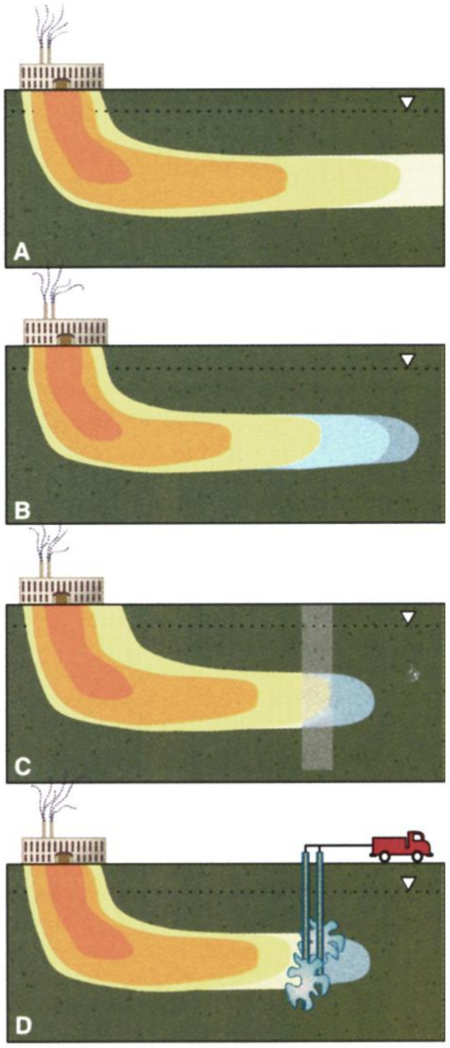
Throughout the world, groundwater is used extensively as a source of drinking water. In the United States, 56% of the population rely on groundwater for their drinking water (*1*). Much of the groundwater extracted in North America and elsewhere is supplied by shallow aquifers, which are susceptible to the release of contaminants from industrial, agricultural, and domestic activities.

A common groundwater contaminant is chromium, which is widely used for electroplating, leather tanning, and corrosion protection (*2*). Chromium is the second most abundant inorganic groundwater contaminant at hazardous waste sites (*3*). On page 2060 of this issue, Ellis *et al.* present a technique for determining the abundance ratio of stable chromium isotopes and apply it to samples from chromium-contaminated sites (*4*). The technique provides an important tool for assessing the migration of chromium from contaminant sources and evaluating the effectiveness of chromium removal systems.

The oxidized, hexavalent state of Cr, Cr(VI), forms chromate (CrO_4^{2-}) or bichromate ($HCrO_4^-$). Chromate-containing minerals are very soluble and, because the chromate ion has a negative charge, chromate adsorption on aquifer minerals is limited (*2*). As a result, chromate may be present at concentrations well above water quality guidelines and may move with the flowing groundwater in aquifers. In contrast, the reduced state, Cr(III), forms insoluble precipitates under slightly acidic and neutral conditions, limiting Cr(III) to very low concentrations in most aquifers (*2*). The reduction of Cr(VI) to Cr(III) thus limits both the concentration and mobility of dissolved chromium. This difference is very important because chromate is toxic and carcinogenic (*5–7*), whereas Cr(III) is a nutrient at trace levels.

Variations in the isotopic ratios of light elements are sensitive indicators of chemical processes that occur in natural systems. For example, the $^{34}S/^{32}S$ ratio in dissolved sulfate increases when bacteria reduce sulfate to sulfide. Ellis *et al.* (*4*) now show that the $^{53}Cr/^{52}Cr$ ratio also changes during reduction of Cr(VI) to Cr(III). They show that abiotic reduction of Cr(VI) resulting from reaction with the mineral magnetite, estuarine sediments, and freshwater sediments leads to a consistent $^{53}Cr/^{52}Cr$ shift. This observation indicates that $^{53}Cr/^{52}Cr$ ratios increase systematically with progressive Cr(VI) reduction in groundwater.

The conventional approach to groundwater remediation is to install a series of pumping wells, extract the water from the aquifer, and treat it with techniques previously developed for surface waters. A series of studies in the late 1980s and early



Groundwater remediation strategies. (A) No attenuation. **(B)** Contaminant removal by natural attenuation processes. **(C)** Contaminant removal using a permeable reactive barrier. **(D)** Injection of a reductant to attenuate the contaminant.

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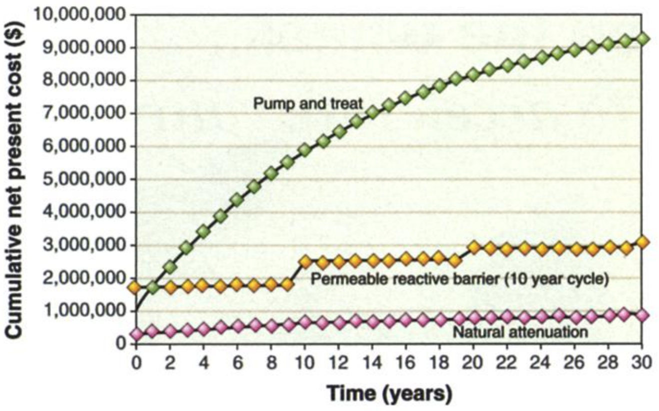
1990s indicated, however, that this "pump-and-treat" approach was expensive and in many cases ineffective (*8*). There are three reasons for this. First, the system extracts and treats clean water along with the contaminated water. Second, full remediation typically takes longer than predicted because contaminants are often retained in fine-grained zones. Third, contaminants that were previously precipitated or adsorbed to mineral surfaces release slowly.



The costs of different groundwater remediation strategies. Natural attenuation, a permeable reactive barrier, and a pump-and-treat system are considered (*14*). This comparison focuses on a halogenated hydrocarbon plume, but the material used in the reactive barrier was zero-valent iron, the same material used to treat hexavalent chromium. The costs are therefore probably similar for a chromate plume.

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Since the late 1980s, research has focused on how to overcome the limitations of the conventional pump-and-treat approach. One possibility is to use the natural ability of aquifers to attenuate contaminants without intervention (*9*). This research has resulted in the development and approval of "monitored natural attenuation" remedies for contaminated groundwater. An alternative approach focuses on the development of in situ treatment systems that clean the contaminated groundwater within the aquifer (*10*, *11*).

Chromate is attenuated naturally because minerals containing reduced forms of iron and sulfur are abundant in many aquifers. These minerals reduce hexavalent chromium to trivalent chromium and promote the precipitation of insoluble solids such as chromium hydroxide (*9*). Organic carbon-rich materials, such as wetland sediments and peat, can also reduce hexavalent chromium. In aquifers where these reduced sediments are abundant and the concentrations of hexavalent chromium are low, the attenuation capacity of the aquifer may be sufficient to prevent chromium migration (see the first figure).

The appropriateness of monitored natural attenuation depends on the groundwater flow system, the rate of chromium migration, and the ability of the aquifer materials to reduce chromate. It can be difficult, however, to distinguish measured chromate decreases caused by attenuation reactions from those caused by mixing or dispersion in the aquifer. At some sites, it is therefore useful to test samples of aquifer materials for the products of chromate reduction.

The measurement of chromium isotope ratios provides a new tool for evaluating the extent of chromate natural attenuation and estimating the rate of chromium attenuation. Relative to conventional methods, it has two advantages: (i) Each ^{53}Cr/^{52}Cr determination provides a measure of the amount of reduction that has already occurred, and there is thus no need to see whether Cr(VI) mass decreases over time. (ii) The measurement of reduction integrates spatially over a flow path, whereas analyses of aquifer solids give information on a much smaller spatial scale.

^{53}Cr/^{52}Cr measurements can also help to evaluate in situ approaches, which have been developed for sites where natural attenuation is insufficient to prevent chromate migration. In situ approaches include permeable reactive barriers, injection of chemical reactants to reduce chromate, and injection of a reductant to react with the aquifer materials to form reduced minerals in the aquifer.

Permeable reactive barriers are constructed by excavating a portion of the aquifer. The aquifer material is replaced with a permeable mixture designed to react with the contaminant (*12*). For inorganic contaminants such as chromium, the reactive material is selected to retain the contaminant within the barrier (*10*). Permeable reactive barriers containing zero-valent iron (iron filings) have been used to treat hexavalent chromium (*10*, *13*).

Landis (*14*) has compared the costs associated with three groundwater remediation options for a 400-feet wide and 80-foot deep contaminant plume: pump-and-treat, managed natural attenuation, and the use of a permeable reactive barrier (see the second figure). The comparison suggests that monitored natural attenuation is least expensive, followed by permeable reactive barrier systems, particularly if the reactive barrier is augmented by natural attenuation. The pump-and-treat system is much more expensive.

Injection of solutions containing strong reductants into aquifers provides in situ treatment alternatives to permeable reactive barriers. A strong reductant such as sodium dithionate can be injected directly into the plume of contaminated water (see the first figure) to promote the reduction of chromate and precipitation of chromium hydroxide. Sodium dithionate solutions also can be injected into the path of a chromate-containing plume to reduce natural ferric iron-bearing minerals, generating a reservoir of ferrous iron-bearing minerals (*15*). These minerals then reduce the chromate as it migrates through the aquifer.

The new finding that ^{53}Cr/^{52}Cr ratios reveal the extent of abiotic reduction suggests that ^{53}Cr/^{52}Cr measurements can assist in the evaluation of the effectiveness of all these approaches to chromate reduction in groundwater.

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