Water scarcity has become a harsh reality in many parts of the world. In the past, water needs were often met by building large dams and importing water over long distances. This approach is proving increasingly infeasible because social and environmental costs are too high (1).

As the increased need for dependable water resources mirrors the growth in population, many communities are turning to reclaimed water to meet their demands. A guiding vision for managing water supplies is to “close the water loop”: Consumers from large cities to individual households use and repeatedly reuse their local water resources, drastically reducing the need to import water. Currently, nonpotable reuse is the most common form of water reclamation. For example, Table 1 summarizes the volumes of water treated for reuse in California in 2002.
But in order to truly close the water loop, we must find publicly acceptable ways of making reclaimed water potable. The most aggressive approach to potable water reuse is direct potable reuse, which has been defined as the “incorporation of reclaimed water into a potable water supply system, without relinquishing control over the resource” (4). Indirect potable reuse, on the other hand, involves mixing the reclaimed water into a river or an aquifer before withdrawing water for treatment and potable reuse. Often, unplanned water reuse already happens when upstream wastewater treatment plants (WWTPs) discharge effluent to rivers that downstream communities use for drinking water. But as new communities develop or as water scarcity becomes truly pressing, regions can plan for indirect potable reuse and intentionally create systems that reuse treated wastewater discharged to a river or percolated into an aquifer.

Planning an effective indirect potable reuse system requires knowledge of the chemical contamination at the intake to the potable-water treatment plant. Armed with this knowledge, the engineers can plan the treatment system accordingly. However, recent studies have identified a worrisome range of contaminants that are often incompletely removed during wastewater treatment and thus could be of concern in an indirect potable reuse system. Researchers in Europe and the U.S. have determined that some pharmaceuticals and human hormones are entering aquatic ecosystems (5–7). In a well-cited paper, Kolpin et al. surveyed 135 streams across the U.S. for the occurrence—not attenuation—of 95 pharmaceuticals, hormones, and personal-care products. They detected 82 compounds at least once, including the major component of birth-control pills (17α-ethinylestradiol), natural estrogens, and other pharmaceuticals from antibiotics to analgesics (8). Although the measured concentrations of these compounds do not seem to put human health at appreciable risk (9), the planners of an indirect potable reuse system would be wise to err on the side of caution and actively try to remove these compounds.

In this feature, we argue that natural processes in rivers can be harnessed to attenuate pharmaceuticals and hormones in water. River attenuation can be a low-cost and ecologically beneficial polishing step in a multiple-barrier approach to water treatment—a method that uses several treatment processes to add redundancy to a treatment system (6). Furthermore, increased public acceptance of the idea is a potential benefit of incorporating river flow into an indirect potable reuse scheme.

In this article, we briefly describe the natural attenuation mechanisms and then discuss recent field studies. Lastly, we review the benefits and drawbacks of river attenuation, as well as areas of further research.

**Natural attenuation and indirect potable reuse**

Models of how a river attenuates biological oxygen demand (BOD) in a wastewater effluent have a long history (10). A growing body of research indicates that natural action in rivers—either incidentally or as part of a planned indirect potable reuse system—can attenuate pharmaceuticals and hormones as well.

The following are the known or postulated physical, biological, and chemical mechanisms that attenuate concentrations of anthropogenic biologically active compounds during river flow. The sum of these mechanisms can represent a treatment process applicable in an indirect potable reuse system as part of a multiple-barrier approach.

**Dispersion and dilution.** Although these processes do not chemically transform a molecule, dispersion and dilution can effectively decrease the peak and average concentrations of a compound. As a consequence, the ambient concentration may not be great enough to elicit an enzymatic or biological response in aquatic organisms. These processes occur in wet regions where large rivers—such as the Mississippi, Rhine, and Elbe—receive wastewater discharges that are diluted by tributaries, but they may be ineffective in dry regions.

**Volatilization.** Most hormones and pharmaceuticals are larger molecules with low Henry’s law constants and tend to reside in the aqueous phase. Thus, volatilization is probably negligible as an attenuation mechanism.

**Sorption.** Solids are ever-present in rivers as stationary sediments; plants; rocks; and, to varying degrees, suspended solids traveling with the flow. The removal of contaminants by sorption to sediment and suspended material can be significant.

**TABLE 1**

<table>
<thead>
<tr>
<th>Types and annual volumes of water reuse in California in 2002</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total freshwater use in California in 2000 was 53,056 × 10^6 m³ (3).</td>
</tr>
<tr>
<td><strong>Type of reuse</strong></td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Agricultural irrigation</td>
</tr>
<tr>
<td>Landscape irrigation</td>
</tr>
<tr>
<td>Industrial use</td>
</tr>
<tr>
<td>Groundwater recharge</td>
</tr>
<tr>
<td>Seawater barrier</td>
</tr>
<tr>
<td>Recreational impoundment</td>
</tr>
<tr>
<td>Wildlife habitat and miscellaneous</td>
</tr>
<tr>
<td>Energy production</td>
</tr>
<tr>
<td>Other or mixed type</td>
</tr>
<tr>
<td><strong>Total</strong></td>
</tr>
</tbody>
</table>

Data in table are from Ref. 2.
but the two processes have very different environmental outcomes. Sorption by sediments leads to a permanent contaminant source, whereas sorption by suspended matter can permanently remove the contaminant from the watershed but deposit it in receiving lakes or oceans. Turbulence can re-suspend and transport sedimentary material, and compounds can sorb to these solids.

A chemical’s structure often dictates the mechanism and magnitude of sorption. Sorption can be an equilibrium process, except when chemical or biological degradation follows or continued diffusion into deeper sediments occurs. At equilibrium, net uptake of the sediments will cease, unless microorganisms adapt and transform the contaminants. In the absence of sediment-mediated (biological or chemical) transformation, sediments can be sources of contaminants. An example of this process is that PCBs accumulate in river sediments with only a slow biotransformation (11).

**Photolysis.** The chemical transformation of a compound by a light-induced mechanism may be either direct or indirect (12). A compound undergoes direct photolysis when a bond within the light-absorbing molecule is cleaved. In indirect photolysis, a photosensitizer, such as natural organic matter, is excited by light, which in turn creates radicals and triplet states that will then react with the compound (13).

**Biodegradation and biotransformation.** Enzymes produced by native bacterial populations can biodegrade or biotransform contaminants in ecosystems. In biodegradation, bacteria grow by using the contaminant as a food and energy source. In biotransformation (co-metabolism), bacteria produce metabolites without gaining energy. Data from river die-away tests can be used to predict biodegradation in flowing water, whereas degradation in sediments requires knowledge of both sediment biological activity and mass transfer due to water–sediment contact. (River die-away tests are microcosm tests used to quantify transformation in river water.) Contaminants may encounter a multitude of microbial habitats and catabolic potentials in waters, including well-oxygenated waters near the surface, oxygenated zones on the riverbed, and anaerobic conditions in stagnant pools and sediments. Whatever the conditions, they must be able to support a population of the microorganism that produces the degrading enzymes (14, 15).

**Examples of river attenuation**

Table 2 presents a partial list of parameters that can be used to characterize a river. These variables can have profound impacts on the existence and scale of attenuation. Each biologically active compound also has its own specific properties; this further complicates the prediction of attenuation from one river to the next. Most of the studies determined that attenuation of pharmaceutical and hormone contaminants occurs over time and distance. However, some compounds appear to persist; these include clofibric acid, a metabolite of several lipid regulators, and carbamazepine, an antiseizure medication (16). An important conclusion is that multiple degradation processes are at work in a river; therefore, a wide range of contaminants can be removed from the water.

The following are significant studies of natural attenuation mechanisms.

**Disappearance of selected anthropogenic compounds during flow in an effluent-dominated river.** The waters of the Santa Ana River in southern California are dominated by WWTP effluent during the dry summer months. The river has a soft-bottom streambed and engineered sidewalls. Gross et al. evaluated natural attenuation of selected pharmaceuticals, metabolites, and endocrine disruptors over a reach of 11 km of river flow, which corresponded to 7 h of residence time (17). The removal of these contaminants through an engineered treatment wetland during this flow was also quantified. The researchers found drops in concentration in the river that ranged from 67% for the lipid- and cholesterol-modifying drug gemfibrozil to 100% for the ibuprofen metabolite COOH-ibuprofen. When the data were normalized with respect to residence times, the researchers found that removal during flow in the Santa Ana River was more efficient than removal during flow through the engineered treatment wetlands. For example, 100% of the gemfibrozil disappeared in the river but only 58% in the wetland. Ibuprofen was reduced by 83% in the river and 47% in the wetland.

**Photochemical and biological degradation of pharmaceuticals during river transport.** In 2005, researchers from our lab continued to study attenuation of pharmaceuticals in the Santa Ana River (18). River-water samples along a 12-km stretch were collected during the day and at night to determine what role photolysis plays in attenuation. Removal percentages of 3 pharmaceuticals—gemfibrozil and
the nonsteroidal anti-inflammatory drugs (NSAIDs) naproxen and ibuprofen—over the 12 km of river flow ranged from 63 to 100%. Naproxen had the largest removal difference between day and night (72–77% at night, 91–100% during the day); this result was confirmed by modeling with GCSOLAR (19). The results indicated that photolysis is not an important attenuation mechanism for ibuprofen and gemfibrozil. Laboratory microcosm studies suggest that biotransformation is the predominant removal mechanism for these two compounds.

**Removal of pharmaceuticals in a river-and-lake system that receives WWTP effluent.** Tixier et al. investigated a system in Switzerland where two rivers, both receiving WWTP effluent, converged into a lake (16). Carbamazepine and clofibrac acid were found to be persistent in the lake. On the other hand, naproxen, ibuprofen, and another NSAID, diclofenac, disappeared with half-lives of 13.8 d, 34.7 d, and 7.7 d, respectively. Earlier calculations had shown that volatilization was not relevant for these compounds but that sedimentation is important for analysis of ibuprofen and diclofenac (20). Other calculations found that phototransformation is a significant removal process for diclofenac, a “possible” mechanism for the NSAIDs ketoprofen and naproxen, unknown for carbamazapine, and not relevant for ibuprofen and clofibrac acid.

**Fate of estrone, estradiol, and 17α-ethinylestradiol in a river that receives WWTP effluent.** Williams et al. (21) studied the discharge of WWTP effluent into rivers in the U.K. by analyzing the effluent daily—1 upstream sample and 4 downstream samples in the Nene and Lea River systems for 28 and 14 d, respectively. Loss rates for estradiol and 17α-ethinylestradiol were not calculated, because estradiol was only found near the detection limit and 17α-ethinylestradiol was only encountered sporadically. For estrone, an average half-life of 2.5 d was observed in the Nene River and 0.5 d in the Lea River. Williams et al. gave biodegradation and sorption as the predominant attenuation mechanisms for estradiol. This conclusion was based on the observation of a shorter half-life for estradiol in the river than what laboratory photolysis studies had suggested (22), paired with the unlikeliness of volatilization. Therefore, the remaining possible mechanisms are sorption and biodegradation.

**Benefits, drawbacks, and risks**
The two major benefits of incorporating river attenuation into indirect potable reuse systems are also two of the greatest concerns for planners of these projects: cost and public acceptance. Expensive advanced treatment processes such as reverse osmosis would probably be necessary capital costs in an indirect potable reuse plan. But the benefit-to-cost ratio of adding river attenuation into a multiple-barrier treatment approach can be very attractive, because a river can remove contaminants with minimal construction, operation, and maintenance costs.

Adding reclaimed water to the natural surface river water might also change the identity of the water in the opinion of the public. People are understandably the most skeptical of potable water, of all the types of reuse (23). However, the average person has a more favorable view of things perceived to be “natural”. If reclaimed water comes into contact with “natural” surface water, such as in a river, then the public will associate a greater degree of “naturalness” with the reclaimed water (24). This view is in part justified by the ability of the river to attenuate pharmaceuticals and hormones. The success of an indirect potable reuse system that incorporates river attenuation might be helped along substantially by combining river attenuation data and a public-relationships message focused on the natural aspects.

Although multiple natural attenuation processes, from photolysis to biodegradation, are at work in a river, they have their limitations. For example, photolysis does not occur at night and takes place slowly on cloudy days, and some pharmaceuticals will be resistant to attenuation mechanisms, as Tixier et al. demonstrated with clofibrac acid and carbamazepine (16). If river attenuation is to be relied upon as one of multiple barriers to contamination in an indirect potable reuse system, then the engineering limitations of the river should be determined and monitored. Systematic testing of the river, focusing on seasonal and diurnal variations, could reveal the river’s reliability and limitations.

Introducing reclaimed water into a river has the added benefit of maintaining riverine habitats. But the ecotoxicology of pharmaceuticals, hormones, and other wastewater-derived compounds is difficult to determine. Typically, toxicology studies focus on individual chemicals, not on the impacts—including the synergistic and additive effects—of the complex mixtures encountered in effluent (25). Similarly, environmental fate studies concentrate on the disappearance of the parent compound, with no emphasis on byproduct formation.

The identification of specific trace contaminants in wastewater, especially bioactive compounds, has proven very difficult. Only ~10% of the organic carbon in wastewater has been characterized in detail (26). The scale and complexity of the problem be-

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**TABLE 2**

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>Flow rate, reach distance, depth, temperature, mixing, turbulence, exfiltration and infiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis</td>
<td>Suspended sediment concentration, solar radiation, photosensitizer concentration</td>
</tr>
<tr>
<td>Sorption</td>
<td>Suspended sediment concentration, suspended sediment settling velocity, sediment fOC (fraction of organic carbon), pH, cation/anion exchange capacities</td>
</tr>
<tr>
<td>Biological</td>
<td>Dissolved oxygen, pH, carbon flux</td>
</tr>
</tbody>
</table>

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come apparent when one considers the large number of intermediates and degradation products—such as metabolites, byproducts, and conjugates of the parent compound—potentially present in reclaimed water. These issues are significant uncertainties; a community would have to evaluate them carefully to find a balance between providing water treatment and managing an aquatic habitat.

Areas of further research
A database that documents the effects of river flow on contaminant attenuation is inadequate to fully describe the potential of natural attenuation. Detailed studies need to be conducted in various settings for a broad range of contaminants, including trace compounds that are of more immediate concern for human health, such as N-nitrosodimethylamine and bromate. These studies should aim to correlate river characteristics with contaminant attenuation so that findings can be extrapolated to other rivers, as has been done for contaminated groundwater. The predictability and reliability of river attenuation as a treatment process needs to be evaluated. Finally, if the use of a natural treatment process like river attenuation improves public perception of indirect potable reuse, then strategies should be developed for communicating the benefits and drawbacks of this approach.

If the caveats are kept in mind, indirect potable reuse is a solution to water scarcity that increasingly makes sense for many regions of the world. Advances in wastewater treatment technology are an important component of this scenario, yet the benefits of harnessing rivers as treatment systems in an indirect potable reuse system are great and should not be ignored. Indeed, with careful research and farsighted policy-making, the sustainable use of water resources and a closed water loop are within reach.

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