# NATURAL BORON CONTAMINATION

The Jordan River, which cuts through Israel and Jordan, largely reflects the scarcity of water in the region. The above picture shows a rare flooding event in the Jordan River in the winter of 2003 at the Baptist site (well-known in Christianity). Just several months later, during the summer of 2003, the river was dry again, as shown below at a site close to Abdall'a Bridge.


**Avner Vengosh, Erika Weinthal, Wolfram Kloppmann and the BOREMED team**

Within the past few decades, the water quality in many of the coastal aquifers along the Mediterranean Sea has rapidly degraded. Overexploitation of the groundwater basins, particularly during the tourist season, has resulted in the lowering of groundwater tables and increasing seawater intrusion into the aquifers. Countries such as Cyprus and Israel have shut down hundreds of wells along the coastline that were used primarily for drinking water.

Facing a shortage of suitable drinking water, these countries have had either to look for alternative sources, such as imported water, or to implement costly technological solutions, such as desalination. In Cyprus, for example, where seawater intrusion is widespread, the water authorities have already established two major desalination plants so that they can supply freshwater to the millions of visitors who arrive every summer. Likewise, Israel is currently building several major desalination plants along the Mediterranean coastline. And in March, Israel's Ministry of Foreign Affairs announced that the country would import 50 million cubic meters of water a year from Turkey over the next 20 years.

But as these well-publicized projects move forward to address salinity in the Mediterranean groundwater basin, another problem looms for residents: boron contamination. Until recently, countries have paid little attention to this and other threats to the quality of the groundwater. Results from an E.U.-sponsored project entitled BOREMED (Boron contamination of water resources in the Mediterranean region: distribution, sources, social impact and remediation) show that boron contamination poses a potential threat to the future use of many groundwater basins along the Mediterranean for the supply of drinking and irrigation water.

Although we know that certain agricultural crops, such as citrus, cannot tolerate high levels of boron, to date we have only limited toxicological data on the impact of boron on human health. Virtually all studies have focused on high-concentration oral exposure of laboratory animals. Boron toxicity had the greatest effect on developing fetuses and testes and, as a result, led to reduced fertility

# N MEDITERRANEAN GROUNDWATER

in the animals.

Yet, prior to the BOREMED project, no clear study on boron and the magnitude of the problem in the water resources in Europe was undertaken. Rather than basing its decision on conclusive scientific evidence, the European Union took a precautionary approach when it promulgated a new boron standard in drinking water in 1998, of 1 milligram per liter.

The BOREMED project, which began in 2001 and ends this spring, is an attempt to integrate different scientific and technological disciplines in order to assess the extent of the boron problem in the southern European and Mediterranean states — in particular, Italy, Greece, France, Cyprus, Israel and the Palestinian Territory. The cases chosen represent both E.U. member states, E.U. candidate states and non-E.U. Mediterranean states and cover both domestic and transboundary aquifers.

**Israel's upstream pumping of the saline groundwater can potentially reduce the salinization rates of groundwater in the Gaza Strip rather than cause downstream harm.**

Specifically, the project aims to map the abundance of boron in Mediterranean water resources, determine its origin, assess its impact on human health and develop possible techniques for its removal from water. Only by understanding the nature of the boron problem can countries devise water management recommendations that can prevent local and transboundary conflicts from arising. Scientific cooperation is the key to water management and policy-making.

## NATURAL SOURCE

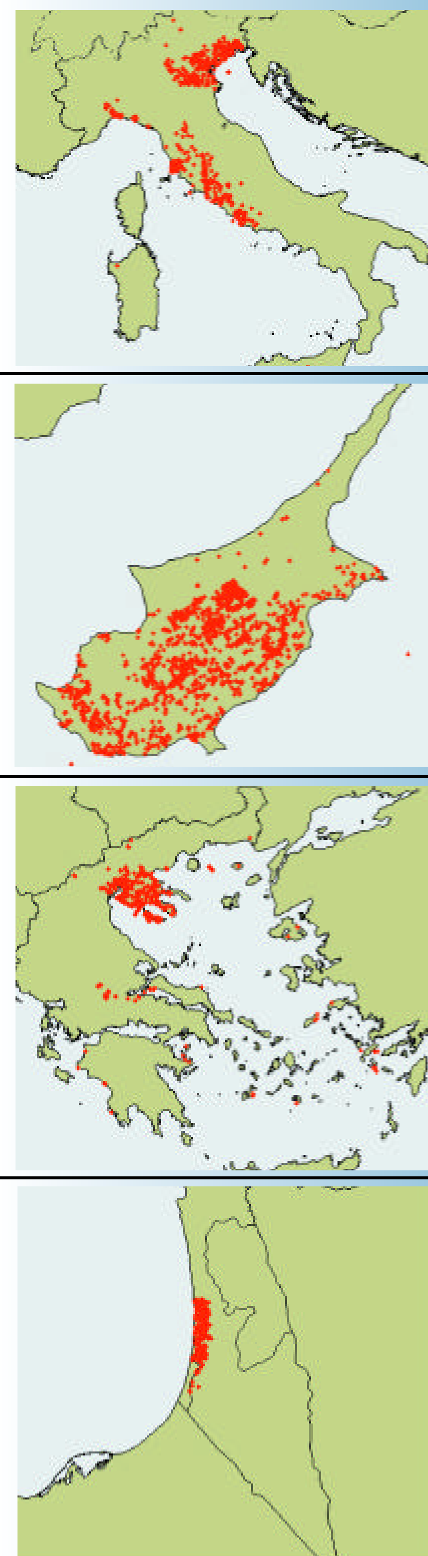
Data collected from more than 6,000 selected sampling points reveal that more than 10 percent of the water resources in the Mediterranean basin have boron levels exceeding 1 milligram per liter, the new E.U. drinking water standard. We found that the highest values of boron are in areas associated with geothermal activity, such as in Tuscany, Italy, and Chalkidiki, Greece. In addition, we discovered high boron levels in the groundwater basins in the central part of Cyprus and in the southern coastal aquifer that is shared between Israel and the Gaza Strip. In order to delineate the origin of boron and salinity in these groundwater basins, we investigated the chemical and isotopic compositions of the boron-contaminated groundwater.

Boron has two stable isotopes that are distributed unevenly among different geological materials and natural water resources. Because different sources of water pollution have unique isotopic fingerprints, we were able to use the boron isotopes to identify clearly the source of the water contamination. For example, the boron isotopic ratios in seawater, wastewater and rocks vary significantly. Thus, when groundwater is contaminated, the imprinted isotopic signature of these different sources is preserved, serving as a tracer for delineating their origin.

Similarly, the application of other isotopes such as oxygen, hydrogen and strontium provide a clue to the origin of the polluted water. By integrating these chemical tools, we discovered that the boron contamination in the Mediterranean groundwater basins is derived primarily from natural processes.

In the Cornia basin in Tuscany, we found that boron leaching from sediments into local groundwater is associated with seawater intrusion, reflecting a complex history of boron uptake and release by clay minerals. In western Chalkidiki, the mixing of groundwater with underlying thermal water rich in boron caused the boron contamination. In Cyprus, water-rock interaction is the main mechanism for the boron enrichment in the water. In the

### AREAS INVESTIGATED FOR BORON CONTAMINATION



Courtesy of Avner Vengosh

**Starting in 2001, the E.U.-sponsored BOREMED project set out to assess the extent of boron contamination in Italy, Cyprus, Greece, and Israel and the Palestinian Territory — shown here respectively from top to bottom — as well as in France, not shown here.**

southern coastal aquifer of Israel and the Gaza Strip, we discovered that boron pollution is associated with the migration of saline groundwater from Israel into the Gaza Strip.

The chemical and isotopic compositions of the groundwater in these studies clearly indicate that the boron problem in the Mediterranean water resources, on the whole, is derived from natural ("geogenic") sources rather than anthropogenic ones.

## WATER TREATMENT

Our results have several implications for the management of national and transboundary groundwater resources in the Mediterranean basin and for the remediation of boron.

Perhaps most importantly, we are challenging the conventional perception that the boron contamination in these countries is a source of human pollution. For years, companies added boron to detergents because it is an excellent bleaching agent — thus resulting in the formation of boron-rich sewage. Moreover, similar to other inorganic ions, boron is not removed during standard sewage treatment processes and even treated wastewater typically has high boron concentrations.

Thus, as a precautionary measure, environmental regulators in both Cyprus and Israel have chosen a particular strategy to reduce boron contamination: mandating regulations that restrict the amount of boron that can be added to detergents. Although the reduction in boron in treated sewage may prove to be beneficial for agriculture because there will be less boron contamination in the irrigation water, these regulations will have negligible effects for improving drinking water.

For a country that soon will join the European Union, such as Cyprus, it will only be able meet its obligation to abide by E.U. standards for drinking water by pursuing an alternative strategy that calls for technological intervention to remove boron. To date, Israel has yet to adopt an official drinking water standard for boron, despite the new proposals for desalination calling for 0.5 milligrams per liter boron in desalinated water. Thus, Israel already faces a similar challenge to Cyprus.

In short, because boron contamination in all our investigated cases comes from natural geochemical background pollution and hence cannot be prevented, the only way to address the boron problem is through treatment of the drinking water.

At present in Italy and Israel, water authorities mix the boron-rich water with high-quality water to reduce the level of boron in the water supplied for both drinking and agricultural purposes. However, the longevity of dilution as a solution is limited, primarily due to the diminishing amount of high-quality water that is available. As a result, our research has focused on the creation of alternative water resources, through the application of technological solutions such as improved desalination and the introduction of new techniques for boron removal from the water.

Reverse osmosis desalination has tremendous potential for a supply of new water for the 21st century, especially in areas of the world where water is scarce or the quality

## WATERING THE DESERT

At the surface, northern Africa is one of the driest places on the planet. But underneath the desert, ancient water lies in a complex groundwater system composed of the Nubian aquifer. Radiocarbon dating techniques have indicated that most Nubian aquifer water is at least 50,000 years old, but a newly developed technique shows that some of the water is 1 million years old — adding further complexity to the Nubian aquifer system, which waters the region.

People have been using the Nubian aquifer water for millennia, collecting water from oases where the groundwater table emerged at the Sahara's surface. But today, the countries that rely on the ancient groundwater for drinking and irrigation water — Libya, Chad, Egypt and Sudan — must do so mostly through pumping because water extraction from the aquifer has lowered the water table. "It's like oil," says Martin Stute, an isotope hydrologist at Barnard College and the Lamont-Doherty Earth Observatory in New York. "It's a precious resource that you pump out of the ground once."

The last time the aquifer recharged substantially was at the Pleistocene-Holocene transition. Dramatic climate changes in the region brought "some major replenishment between 5,000 and 7,000 years ago," says Mike Edmunds of the Oxford Centre for Water Research, who has worked in Libya since the 1960s and has radiocarbon-dated water in the region. Isotope signatures from noble gases and oxygen-18 indicate that melting ice caps and a rise in sea level led to intensification of the monsoon over central parts of the Sahara, he says, which led to higher rates of precipitation and recharge to the aquifer.

More recently, human settlement and agriculture have relied on old water from the aquifer for survival. Since the 1980s, Libya has built an immense water delivery system, laying 4-meter-diameter pipes deep in the desert to deliver water to cities in the north. In a region that receives less than 20 centimeters of rainfall a year, the pipeline now delivers half a million cubic meters of water a day, according to UNESCO, which estimates that the entire aquifer holds 120,000 cubic kilometers of water — comparable to a several-hundred-meter-deep pool the size of California.

Egypt now uses its desert oases as well sites, says Neil Sturchio of the University of Illinois at Chicago. Pumped wells send water flowing over cultivated fields for 8 to 12 hours a day, spilling groundwater that accumulated over eons onto the surface — to evaporate in a day.

Neil Sturchio

**Zheng-Tian Lu, a physicist at Argonne National Laboratory in Illinois, inspects an artesian well at Farafra Oasis, in the Western Desert of Egypt. Lu led research that dated the oldest water in the Nubian aquifer, which sits under Egypt, to about 1 million years old.**

Sturchio and his co-workers took advantage of some of those Egyptian oasis wells to collect dissolved gases from the groundwater, in order to perfect a new method of dating water using the rare isotope krypton-81. The team, composed of researchers from several institutions, including Argonne National Laboratory in Illinois, the University of Bern in Switzerland, and Ain Shams University in Cairo, extracted gases from 1,000-liter samples of water at several Egyptian sites. Using a recently developed method called Atom Trap Trace Analysis, they found that the oldest water samples carrying krypton-81 had entered the aquifer about 1 million years ago, the team reported in the March 12 online edition of *Geophysical Research Letters*.

"This is a technique that we have been after for 15 years or longer," Stute says. Krypton-81 is hard to measure because of extremely low concentrations, at thousands of atoms per liter, and earlier methods were cumbersome and inconclusive, he says. The new method with krypton-81, Stute says, "opens doors and allows us to look beyond the radiocarbon window," which is limited to 40,000 years or so.

However, Stute says that he would like to have seen radiocarbon dates for the samples the team took for further comparison. Much younger ages for the water collected could still be true, he says, because of potential mixing of different-aged water flows in the complex aquifer basins, which might affect the various dating techniques differently.

Edmunds agrees that mixing may skew the measurements. Another problem with the method, he says, is that molecular diffusion will dampen out the krypton-81 signal, giving the method a precision of plus or minus 1,000 years. For more recent groundwater shifts, he explains, that loss in accuracy makes dating specific events more problematic, particularly for the Pleistocene-Holocene transition in the region. Edmunds says, however, that the results are "convincing" and promising for future use in studying the paleoclimate record.

In the end, scientists say that dating the water in the Nubian aquifer may not have a direct impact on water resources management. "Whether it's 50,000 or a million years old, it doesn't change much. That water is nonrenewable on a human time scale," Sturchio says. However, knowing that reality "may change how people decide to use it," he says.

In Libya, researchers from the United Nations Development Programme and the International Energy Foundation say that most industrial users do not recover and reuse water, and they cite a growing desire for greater efficiency and effective management of water use. Without any substantial recharge to the system, and at the current rate of consumption, particularly in Egypt, Sturchio says, the ancient water available from the aquifer could be gone in 100 to 500 years.

**Naomi Lubick**

Zheng-Tian Lu

is inadequate. Its widespread application, however, is hampered by the fact that reverse osmosis desalination does not remove boron sufficiently (only 60 percent). As a result, desalination of seawater does not reduce the boron level below the new standard for drinking water in the European Union (and will be also problematic for the non-European Mediterranean countries adopting a similar drinking water standard for boron). Therefore, additional removal techniques must be introduced in order to bring boron levels down to drinking standards.

Different partners in the BOREMED project have developed several independent methodologies for removing boron from water. In Cyprus, BOREMED partners have utilized boron-specific resins combined with a small-scale reverse osmosis to reduce the amount of boron in the groundwater for local users. In Israel, BOREMED partners have succeeded in removing boron by optimization of reverse osmosis processes such as multi-step desalination. Other partners from the Netherlands have established a new method of boron removal through co-precipitation with hydroxides. In addition, a joint Israeli-Turkish team invented a new technique for boron removal through reacting seawater with fly ash and coal materials. This method is particularly useful in Mediterranean countries such as Turkey, where fly ash is abundant and cheap.

# NATURAL CONTAMINANTS

Boron is only one of many geologic materials that occur naturally in the environment and can pose health risks to people. Geoscientists are actively involved in studying such substances by monitoring groundwater, surface water and soils, and by mapping their distributions. The findings may help policy-makers devise new strategies for regulation and mitigation. Below, we give a snapshot of several well-known potentially toxic earth materials found around the world and the current U.S. policy for each. Visit **www.geotimes.org** for links to past *Geotimes* coverage and other online resources.

| CONTAMINANT | SOURCES | OCCURRENCE | HUMAN HEALTH EFFECTS | U.S. POLICY ACTION |
|---|---|---|---|---|
| **ASBESTOS** | ■ Serpentinites and amphibolites<br>■ Most common in insulation products in a form called chrysotile | Naturally occurring around the world and still mined in Brazil, Canada, China, Kazakhstan, Russia, Zimbabwe and elsewhere | ■ Asbestosis (lung scarring that impedes breathing)<br>■ Mesothelioma (only attributable to asbestos exposure)<br>■ Lung cancer | Onsite containment is now considered preferable to removing asbestos, which is no longer available for use in building insulation in the United States but may be present in roofing materials and other products. |
| **RADON** | ■ Uranium decay in rocks and soil<br>■ Atmospheric radiation | Present in soil and other bedrock, often beneath homes that might trap radon gas | ■ Lung cancer risk from exposure to small amounts | New housing construction methods prevent the entrance of radon, and monitoring indicates whether remodeling and retrofitting of older homes is necessary, to remove the gas with fans. |
| **MERCURY** | ■ Cinnabar and other mineral deposits<br>■ Also released in volcanic emissions and human activities like fossil fuel combustion | Naturally occurring elemental metal, mined mostly in Algeria, Kyrgyzstan and Spain (major deposits are also in Italy, and the United States has smaller reserves) | ■ Mercury poisoning (sometimes associated with fish consumption), which can lead to neural disorders and sometimes death | Power plants, incinerators or other sites with burning must control or avoid release of mercury into the air, and legislation is under consideration to limit use in everyday products such as dental fillings. |
| **ARSENIC** | ■ Soil, rocks and water that contacts them<br>■ Present in wood treatments<br>■ Released in fossil fuel burning, agricultural uses and metal production | Naturally occurring in metal ore deposits such as copper-gold and lead, in Peru, Canada and elsewhere; also released in coal burning | ■ Increased risk for various cancers, such as skin and bladder<br>■ Breathing and heart irregularities | No policy is in place other than standard allowable levels set by the Environmental Protection Agency (EPA). |
| **CRYSTALLINE SILICA** | ■ Crystalline quartz from continental, crustal, volcanic and other rock types | Ubiquitous — present in granite, potting soil, bricks and clays, among other substances | ■ "Miner's asthma" or silicosis, from scarring of lung tissue by inhaled quartz shards, which may lead to lung cancer | Occupational Safety and Health Administration (OSHA) regulates workers' exposure to breathable crystalline silica (as dust or other particulate matter). |
| **BORON** | ■ Boric acid, boron oxide and borate salts<br>■ Typically used in cleansers, housing materials such as fiberglass and ceramics | A trace element that leaches from rocks, especially in geothermal regions; also occurs naturally in borate salts from brine as well as in underground mines | ■ Nose, throat and eye irritant if breathed in moderate amounts<br>■ Other human effects are unknown, though long-term exposure may produce negative reproductive impacts | EPA does not regulate boron in water, but it does monitor it in foods, and OSHA sets standards for workplace exposure. |

Sources: EPA, OSHA, U.S. Geological Survey

Each of the new different methodologies has its own benefits and costs. Ultimately, the E.U. countries that face a boron problem will have to adopt one of these new technologies in order to be in compliance with the new drinking water standard for boron.

## CROSSING BOUNDARIES

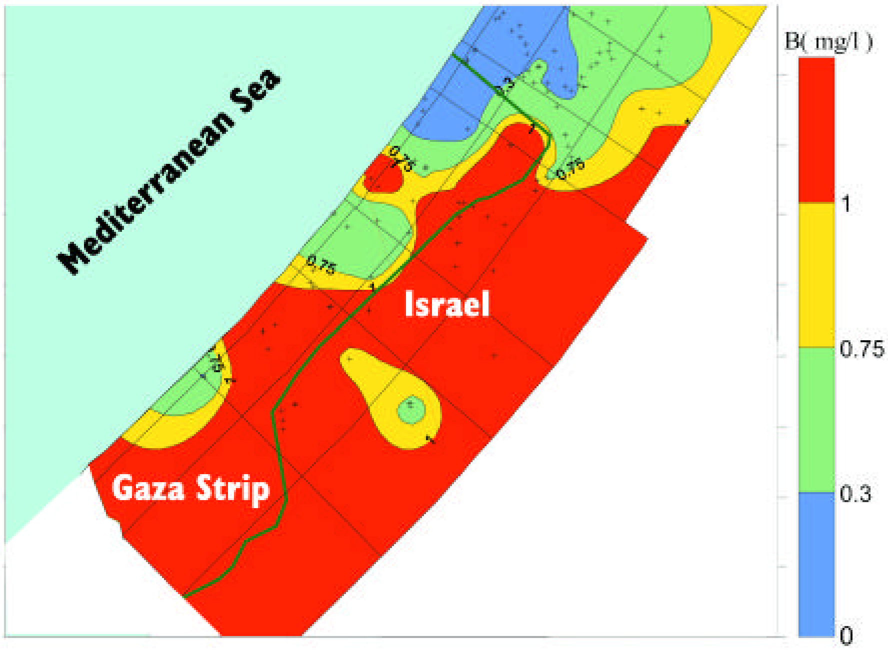
Through an integration of geochemistry, hydrogeology, numerical modeling and policy analysis, we also have devised a potential management solution to the water crisis in the Gaza Strip. The local aquifer underlying the Gaza Strip is perhaps one of the most stressed resources in the Mediterranean basin in terms of water quantity and quality: Chloride concentrations reach 1,500 milligrams per liter (six times the E.U. standard); nitrate concentrations reach 400 milligrams per liter (eight times the E.U. standard); and boron concentrations reach 3.5 milligrams per liter (more than three times the E.U. standard).

Over the past five decades, the amount of water pumped from the Gaza aquifer has far exceeded the natural water replenishment. As the water level has declined, the water quality has become unsuitable for human consumption, owing to the high levels of salinity, boron and nitrate pollution. Nevertheless, more than 1 million people depend entirely upon this aquifer for drinking and irrigation water.

Our chemical and isotopic data show that most of the salinity phenomenon in the Gaza Strip is derived from flow of natural saline groundwater from Israel towards the Gaza Strip. As a result, the southern coastal aquifer does not resemble a classic "upstream-downstream" dispute over a transboundary aquifer: Israel's upstream pumping of the saline groundwater can potentially reduce the salinization rates of groundwater in the Gaza Strip rather than cause downstream harm.

Numerical simulation of different pumping scenarios confirms our hypothesis that increasing pumping along the Gaza Strip border combined with desalination and supply to the Gaza Strip, as well as moderate reduction of pumping within the Gaza Strip, would improve the water quality of groundwater there. Moreover, our finding that the salinity problem in the Gaza Strip is partially natural de-politicizes the water issue and offers a practical solution for the water crisis in the Gaza Strip that has win-win benefits for both the Palestinian Territory and Israel.

## BORON DISTRIBUTION IN THE SOUTHERN COASTAL AQUIFER (SUMMER 2000)




Courtesy of Avner Vengosh

**The BOREMED project has mapped boron distribution in groundwater from the southern Mediterranean coastal aquifer and the Gaza Strip. The different colors represent boron concentration in milligrams per liter. In most parts of the aquifer and the Gaza Strip, the boron concentration exceeds the drinking standard of I milligram per liter for the European Union.**

## CLEARING THE WAY

The promulgation of a new drinking water standard for boron in the European Union has forced both E.U. member and non-member states to address boron contamination in drinking water even before a strong causal link has been found between boron contamination and health effects. Yet, while new technologies now exist for boron removal, the adoption of this new drinking water standard is complicated by the fact that each country faces different institutional constraints.

In Italy, the boron problem is a local problem rather than a national one, and as a result, the end-user in conjunction with the regional water authority is responsible for developing its own program for boron removal. In contrast, in the coastal aquifer that is shared between Israel and the Palestinian Authority, the boron and salinity problem will only be resolved through the development of institutions for international cooperation. Finally, in Cyprus, the boron problem is a national problem, thus requiring a national solution instead of a local or international solution.

In the end, the ability to address the boron problem at the local, national and international levels in the Mediterranean basin will depend entirely on an integration of science, technology and policy.

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