

PATRICE PETRO

# Editor's Note



The Center for International Education is pleased to introduce its 2015/2016 Global Studies Research Fellows: Professors Lane Hall (English), Jenny Kehl (Center for Water Policy), Oriol Miroso (Sociology), Michael Nosonovsky (Engineering), and James Wasley (Architecture). The research collected in this volume of *Intersections* is made possible by the work of our Fellows addressing this year's theme: water-centric cities. To understand the water-centric city is to know it in its most transdisciplinary sense: water consumption, conservation, urban distribution, equity issues, pollution and toxic run-off, and strategies for

responsible governance. Over-consumption and climate change threaten water scarcity, and this is felt keenly in cities, our largest consumers of both food and energy. Global cities are developing strategies to address the increasing demands on their water systems as well as issues of inequity in development. Join us at our conference in April, where we will re-define water-centric cities, address planetary limits, challenge current consumption patterns, and develop alternative strategies to promote global resource stewardship. We will examine water scarcity, food security, and energy production, and we will analyze global issues as well as city-level policy reforms to improve water management in the interest of regional stability, global security, and economic and environmental sustainability.

A handwritten signature in black ink, appearing to read "Patrice Petro". The signature is fluid and cursive, with a large initial "P" and a long, sweeping underline.

Patrice Petro - Vice Provost for International Education

MICHAEL NOSONOVSKY

# Biomimetic Materials and Surfaces

## Water-Related Applications for Water-Centric Cities

Due to their location on water shores, cities such as Venice, Milwaukee, St. Petersburg, or Rio de Janeiro throughout history served as centers of international commerce and communication and became catalysts of cultural, technological, social and economic development, which often shaped nations and economic systems as we know them today.

Modern global economic and demographic developments coupled with environmental concerns and global climate changes in recent decades have raised new concerns and challenges for water-centric cities. Among these challenges are the utilization of urban drainage and wastewater, environmental pollution, lack of sustainable energy and high carbon footprint due to transportation, industry, construction, energy production, and other activities of these megalopolises.

New solutions are needed to meet these new challenges. In particular, the so-called “fifth paradigm” has been suggested to achieve sustainable integrated urban water, energy, drainage, and

transportation infrastructures [1]. In this approach, the urban infrastructure, resilient and hydrologically/ecologically functioning landscape and water resources constitute one system. However, it is very challenging to implement such an approach.

We have suggested a potential new solution: biomimetics [2-8]. Biomimetics is a growing area of multidisciplinary engineering and fundamental research that is defined, according to the Merriam-Webster dictionary, as “the study of the formation, structure, or function of biologically produced substances and materials and biological mechanisms and processes especially for the purpose of synthesizing similar products by artificial mechanisms which mimic natural ones.” In a broader sense, biomimetics (also called bionics or biomimicry) is the imitation of the models, systems, and elements of nature for the purpose of solving complex human problems. A biomimetic approach could be naturally integrated with the new sustainable urban paradigm for water-centric cities.

## **Biomimetics in Surface Science**

One particularly interesting and rapidly expanding area of biomimetics is biomimetic materials and surfaces. Surface science is an important area of the materials science, because properties of any material at its surface are often different from the properties in the bulk. A famous physicist, Wolfgang Pauli, once said: “if God made bulk material, surfaces were invented by the

devil.” Surface properties are particularly important when one deals with very small objects or devices, say, in nanotechnology. The bulk forces are proportional to the volume, which is the third power of the linear size of a device,  $V \sim R^3$ , while the surface forces are proportional to the surface area, which scales as the second power,  $A \sim R^2$ . Therefore, when one is trying to build a very small device, the surface-to-volume ratio grows,  $A/V \sim R^{-1}$ , and surface forces, such as the friction and adhesion, become very strong and dominate over other forces. This is why it is very important to learn how to control the surface forces in order to build novel devices, many of which are supposed to be miniature in size.

Fortunately, the advances in nanotechnology also provide new tools to control the surface structure. Here at the University of Wisconsin-Milwaukee, we study how to control surface profile in order to obtain desirable adhesion properties. Part of this is superhydrophobicity, or the ability of certain cleverly engineered surfaces to repel water. Superhydrophobic surfaces also tend to repel dirt, and the latter property is called “self-cleaning.” Interestingly, scientists learned about superhydrophobicity from plants. For centuries, the lotus (*Nelumba*) was a symbol of purity in India and China, because its leaves emerge clean and dry from muddy water. The lotus is shown in many ancient Buddhist and Hindu paintings, where it served as a symbol of both material and spiritual purity. An ancient Hindu poem, Bhagavat Gita, says about the seeker of truth: “Having abandoned attachment, one acts unattained by evil, just as a lotus leaf is not wetted.”



**Figure 1: (Left) Painting of Hindu god Vishnu sitting on Lotus. (Right) Lotus leaves emerging from water.**

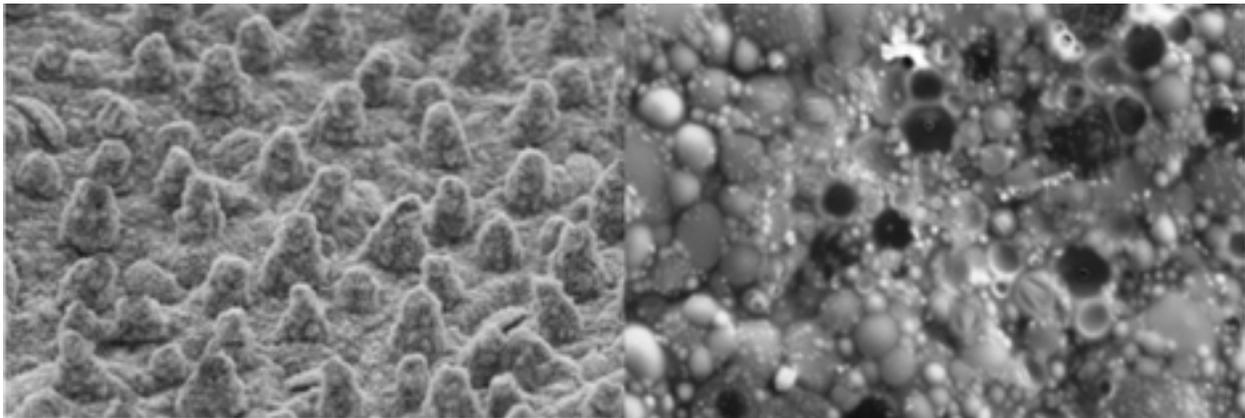
Only about 20 years ago, when new types of microscopes were invented, scientists learned why the lotus repels water and dirt. It turned out that leaf's surface has a complex hierarchical structure: there are microscopic bumps (called papillae), upon which there is a layer of wax with much smaller, sub-micron scale (nanoscale) bumps. None of these three factors—microbumps, nanobumps, and wax—results in superhydrophobicity when taken separately. However, when combined together in a proper way, they lead to the “lotus effect,” i.e., superhydrophobicity and self-cleaning.

After the lotus effect was discovered in plants in the 1990s, engineers in many labs in the world started to mimic the lotus leaf surface for artificial surfaces made of metallic, polymeric, ceramic,

and all kinds of other materials. This is because new technologies to produce micro- and nano-patterned surfaces, such as nanolithography, also emerged at about that same time. These efforts at biomimetic mimicking of living nature for engineering applications have resulted in new, commercially available products. Furthermore, the lotus effect led to novel underwater self-cleaning oleophobic (i.e., repelling organic contaminants) coatings used in water applications such as water pipes to reduce biofouling (accumulation of undesirable microorganisms and organic contaminants), as well as novel icephobic coatings. On the basis of the lotus effect and superhydrophobicity, new similar effects were found or suggested, including non-adhesive “omniphobic” surfaces (which repel everything, both water and organic liquids), new types of filtering membranes, new biomedical devices to reduce blood stagnation, icephobic surfaces, and many others. A number of these have direct application to water industry, including self-cleaning pipes and water components such as water heaters and meters, which we are developing here at UWM in collaboration with local companies.

The research on superhydrophobicity involves both experimental studies and theoretical modeling in order to understand how exactly superhydrophobicity works, and why hierarchical organization of surface bumps, with the surface nanoroughness imposed on top of the microroughness is needed, as well as to optimize surface roughness.

One particularly important direction is water-repellent materials for civil infrastructure, such as concrete and asphalt. Traditional concrete is hydrophilic and it absorbs water, which is unfortunate because it reduces the lifespan of concrete structures, especially when they undergo the freezing-melting cycle in cold climates like Wisconsin. However, by adding specially tailored nanoparticles into the concrete admixture, the concrete may become hydrophobic and superhydrophobic, which has been demonstrated here at UWM in Professor K. Sobolev's lab [3]. Such concrete is much more durable than the conventional variety (Figure 2), and it is of interest for civil infrastructure in water-centric cities.



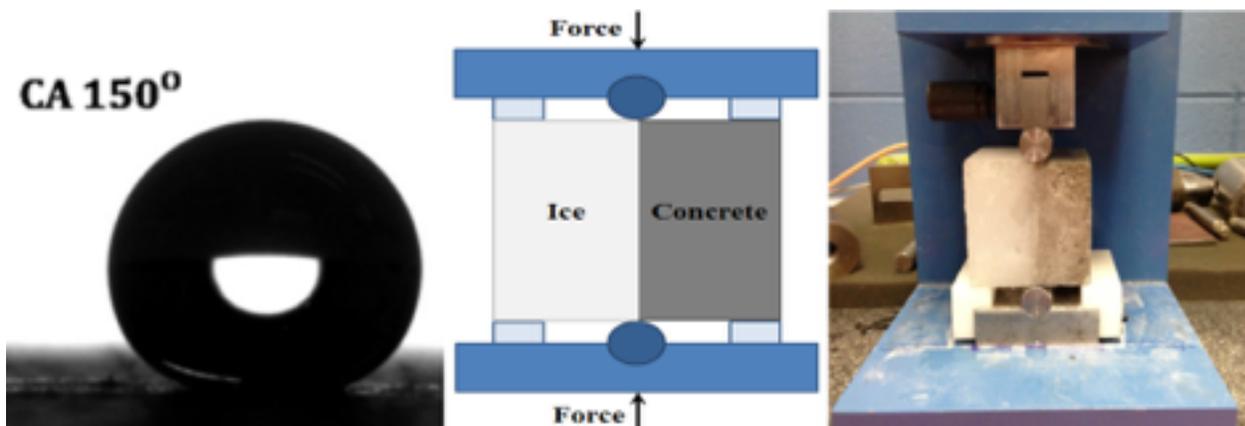
**Figure 2: Scanning Electron Microscope image of a lotus leaf showing hierarchical surface roughness (left) and lotus-inspired superhydrophobic concrete synthesized at UWM (right) [3].**

## **From Hydrophobicity to Icephobicity**

Superhydrophobicity and related phenomena have been studied actively for more than a decade; now scientists are at work

broadening the scope of applications of the phenomenon. Besides the superhydrophobic concrete, we want to understand how superhydrophobicity can be used for corrosion resistance and to repel ice. Generally speaking, we'd like to understand how a surface roughness pattern and/or vibrations (which constitute a temporal pattern) can be used to affect phase transitions.

From the point of view of a chemist or physicist, water has very unusual properties. Water is denser than ice, and it expands when it freezes. Additionally, water exhibits an unusual type of molecular interaction called “hydrophobic interactions.” However, if water is unusual, ice is even more interesting and complex than water. Just think about the complex shape and symmetry of a snowflake (an ice crystal) in comparison with a spherical water droplet! If we understand the fundamental mechanisms of how hierarchical surface roughness can control water adhesion to solids, the next step is to deal with ice adhesion (Figure 3). Icephobicity has many potential applications especially in such a place like Milwaukee, Wisconsin, where the climate is cold in the winter, and a water-centric city becomes a snow-centric city!

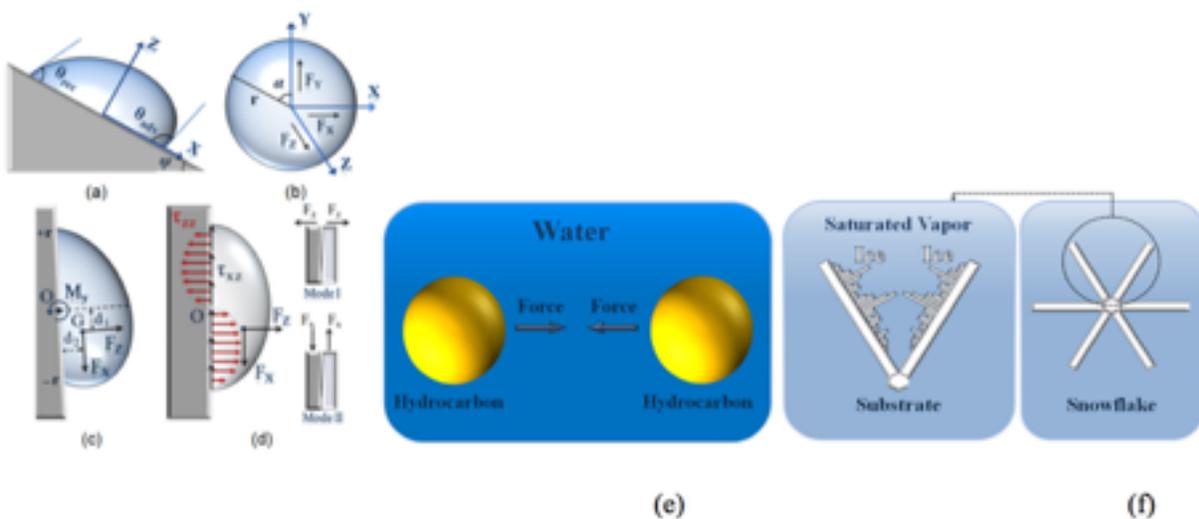


**Figure 3: A water droplet on a superhydrophobic concrete surface forms almost a sphere due to water repulsion from the surface (left). A setup to study ice adhesion to concrete, schematic (center) and photo (right) [3].**

| Property                                  | Water  | Ice   |
|---|--|---|
| Definition of "phobicity"                 | Low surface energy/low adhesion<br>High contact angle<br>Low CA hysteresis<br>Bouncing-off                               | Low adhesion<br>Low normal strength (maximum stress)<br>Low shear strength<br>Bouncing-off supercooled droplets |
| Interaction                               | Hydrophobic interaction  | Crystallization of ice and snowflakes   |
| Thermodynamic relationship                | Minimization of $\Delta G = \Delta H - T\Delta S$  | Surface roughening transition $\Delta G = \Delta H - T\Delta S = 0$ and similar                                 |
| Typical manifestation of the interactions | Hydrocarbone molecules in water environment  | Ice molecules in saturated vapor environment at negative temperatures   |
| Effects                                   | Protein folding (including fractal shape), self-organized criticality, long-range hydrophobic force, wetting transitions | Snowflakes (diverse but symmetric, fractal)   |

**Table 1: The comparison of hydrophobicity and icephobicity [10].**

Preliminary results are consistent with the concept of the parallelism between the definitions of superhydrophobicity and icephobicity, which we have suggested earlier (Table 1). The analytical study will expand this concept in order to provide a solid thermodynamic definition of icephobicity (Figure 4).



**Figure 4: (a) Water droplet on a tilted surface and (b) forces acting upon the droplet; (c) ice attached to a solid surface and (d) forces acting upon ice. It is noted that CA hysteresis mostly controls the droplet detachment, whereas ice detachment is similar to the mode I/II fracture [9]. Parallelism of hydrophobic interaction and ice formation. (e) The attractive force between hydrophobic molecules (hydrocarbons) is a result of Gibbs energy  $\Delta G = \Delta H - T\Delta S$  minimization due to entropy increase  $\Delta S$  in water molecular network (hydrocarbon-water-hydrocarbon system) prevailing over enthalpy  $\Delta H$  (b) The synchronization of branch growth during formation of a snow crystal due to  $\Delta S$  prevailing over  $\Delta H$  (ice-saturated vapor-ice system) [10].**

One particular biological source of inspiration for research into icephobicity are the so-called thermogenic plants, which generate heat and can melt snow. The lotus is a thermogenic plant in addition to being superhydrophobic, so the relationship between the thermogenic and superhydrophobic properties is a matter of investigation. Other thermogenic plants include somewhat exotic flowers like the tropical *Amorphophallus titanum* (so named due to the unusual shape of its flower reminiscent of a gigantic phallus) and the skunk cabbage (*Symplocarpus foetidus*), which produces a pungent but not harmful odor, the source of the plant's name. The latter plant is common in the North America, including Wisconsin where it can grow through snow in the early spring. The snow-melting properties of the skunk cabbage and microstructure of its leaf have become an object of our investigation, [11] and an inspiration for biomimetic, icephobic materials (Figure 5).



**Figure 5: (a) the leaf of skunk cabbage enclosing spathe and spadix, and (b) the spathe. (c) Skunk cabbage as observed in its natural environment in wet land (Schlitz Audubon Nature Center, Milwaukee, WI) in the month of November (d) Scanning electron micrographs of skunk cabbage leaf (e) *Amorphophallus titanum*, a tropical thermogenic plant [11].**

## **Other Water-Related Biomimetic Applications**

Besides the lotus effect, there are many other amazing biomimetic effects, including gecko adhesion, the shark-skin effect, the rose-petal effect, and many others.

The shark skin effect is the reduction of hydrodynamic drag due to the special microstructure and orientation of riblets found in shark skin. The shark-skin surface suppresses turbulence (chaotic flow leading to excessive friction) in flowing water, and thus reduces energy loss and water resistance (drag). Biomimetic swimsuits using the shark skin effect have already been produced for swimming competitions and various water applications (from

ships and submarines to water pipes). Biomimetic membranes utilizing the lotus effect are used for desalination and separating oil from water. A mesh formed by a material which is hydrophilic but superoleophobic (repelling oil and organic liquids) or, vice versa, superhydrophobic but oleophilic would let water (but not oil) through and can be used for water-oil separation. A similar type of membrane (involving reverse osmosis) can be used for desalination [12].

There are many other biomimetic effects potentially applicable to the water industry and water-centric cities. Superhydrophobic corrosion-resistant coatings are being developed at UWM [13]. Note that biomimetic solutions mimic living nature and thus are environmentally friendly. For example, traditional antifouling coatings for ship hulls involve paints, which are toxic and kill microorganisms, while biomimetic coatings are environmentally benign and thus meet environmental standards for ports. It is therefore very important to integrate biomimetics with ecology. Toward that end, a deeper view of biomimetics is needed that will cover not just its engineering and technology aspects, but also the broader philosophical, historical, and social aspects of biomimetics.

## **Philosophical, Historical, and Social Implications of Biomimetics**

While biomimetic approaches are embraced by engineers and

applied scientists, the fundamental philosophical and societal implications of biomimetics remain much less understood, thus limiting the transformative potential of the biomimetic paradigm for society at large. Biomimetics has a long history. The word “biomimetics” was coined in the 1950s by the biophysicist Otto Schmitt, and was popularized in the 1970s. However, the idea of mimicking nature for artificial devices has existed since antiquity (for example, the idea of mimicking bird wings for men to fly in the myth of Icarus and the “robot”-like heroes such as the Golem) [2]. The reason biomimetics has remained popular since the 1970s is related to the increasing popularity of various “holistic” concepts.

The dominating attitude of humans toward nature since the 19th century and until the mid-1900s was the belief that science and technology would eventually provide almost unlimited power to conquer and transform nature in a way comfortable to humans (e.g., plans to turn rivers and move mountains, etc.). Fueling this perception of the nature-human relationship was the tremendous successes of empirical science and technology since the scientific and technological revolution in the 17th century, and especially since 1900. However, in the second half of the 20th century, it became obvious that it is not possible to solve many economic and social problems just by attempting to conquer nature. The human-nature relationship is much more complex, and humans can benefit by learning from living nature rather than trying to change it. As a result, new areas such as “ecology” and “holism,” which emphasize the harmony between humans and nature,

became increasingly popular. The emergence of biomimetics is a part of this trend.

It is not by chance that engineers and materials scientists started to pay attention to nature. This reflects a more general trend. During most of the 20th century, much technology was developed under the assumption that humans would eventually be able to transform nature in any way they wanted. Later humans understood that there is a lot to learn from nature. Traditional engineering approaches imply that you have an exact blueprint of your final product and an exact procedure how to make it. Living nature is very different. It has only general algorithms encoded in the DNA and hierarchical self-replicating structures, which adjust to the changing environment when they grow. So, instead of concentrating on a rigid homogeneous structure and on an exact solution to a problem, the biomimetic paradigm provides a much more flexible and holistic view.

A similar change of paradigm has occurred in many areas of science; in physics and mechanics new concepts such as fractals were suggested to study phenomena which are not described by continuous functions and traditional calculus. More importantly, the very difference between natural and artificial (nature and nurture), becomes elusive. The biomimetic approach is an example of that. Interestingly, in social studies and humanities this trend is even more pronounced. Our colleagues from social studies state that in the world of circulating cultures and accelerating human movement, all ideals of homogeneity have

become irrelevant. This new way of thinking, which biomimetics brings, encourages better harmony between humans and nature. If something mimics nature, it is also ecological. Together with colleagues, we have identified biomimetic surfaces as one of the three areas of ecotribology (or “Green Tribology,” tribology is the study of friction) [7-8].

At an even more fundamental philosophical level, one can view the transformative scientific revolution of the 17th century, which resulted in the development of the modern empirical scientific method, as the abandonment of Aristotle’s approach towards nature as expressed in his physics and metaphysics [6]. The new empirical method, as developed by Francis Bacon, Isaac Newton, Descartes, Leibnitz and other great minds of the 17th century, has led to the establishment of modern science, which resulted over the subsequent 300 years in an amazing number of discoveries and the transformative technologies of modernity. However, it became evident by the second half of the 20th century that such a “technocratic” approach also has its own limitations, leading to post-modern views on nature and humankind. The emergence of holistic approaches (including biomimetics) followed the same trend.

## **Conclusions**

The UWM Global Fellows program has provided me a unique opportunity to concentrate on these broader aspects of

biomimetics that are beyond standard engineering topics but are nonetheless of great significance. However, on a more practical side, biomimetic materials which repel water, ice, and other substances, or resist corrosion, provide cheaper solutions and reduce maintenance costs such as cleaning, which eventually improves the quality of life of all residents of water-centric cities.

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## Images

Figure 1: “Vishnu.” 1730. The Government Museum and Art Gallery, Chandigarh. Wikimedia Commons. Public Domain. <https://commons.wikimedia.org/wiki/File:Vishnu.jpg>; and “Lotus Field.” 2009. Rebexart. Wikimedia Commons. Used under Creative Commons License Share-Alike 3.0 Unported. [https://commons.wikimedia.org/wiki/File:Lotus\\_field.jpg](https://commons.wikimedia.org/wiki/File:Lotus_field.jpg).

Figure 2:

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Figure 3:

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Figure 5: R Ramachandran, M Nosonovsky, “Surface micro/nanotopography, wetting properties and the potential for biomimetic icephobicity of skunk cabbage *Symplocarpus foetidus*,” *Soft Matter* 10 (2014), 7797-7803 – Published by the Royal Society of Chemistry. Licensed under a Creative Commons Attribution 3.0 Unported License.



**Michael Nosonovsky** is Associate Professor of Engineering at the University of Wisconsin-Milwaukee. His research focuses on tribology (the study of friction) and the surface sciences, bio-mimetic materials and water-related physicochemical surface phenomena such as wetting, capillary force, and adhesion, as well as the mechanical properties of omniphobic substances, including self-healing, self-lubricating, self-cleaning compounds. His recent publications include *Tribology for Scientists and Engineers* (2013) and the forthcoming *Friction-Induced Vibrations and Self-Organization: Mechanics and Non-Equilibrium Thermodynamics of Sliding Contact*.

Center for International Education

# Water-Centric Cities Conference

Edith S. Hefter Conference Center, April 15-16, 2016

To understand the water-centric city is to know it in its most transdisciplinary sense: water consumption, conservation, urban distribution, equity issues, pollution and toxic run-off, and strategies for responsible governance. Over-consumption and climate change threaten water scarcity, and this is felt keenly in cities, our largest consumers of both food and energy. Global cities are developing strategies to address the increasing demands on their water systems as well as issues of inequity in development. Join us at our conference in April, where we will re-define water-centric cities, address planetary limits, challenge current consumption patterns, and develop alternative strategies to promote global resource stewardship. We will examine water scarcity, food security, and energy production, and we will analyze global issues as well as city-level policy reforms to improve water management in the interest of regional stability, global security, and economic and environmental sustainability. The conference will feature presentations by 20 distinguished scholars from the US and abroad, and will take place Friday and Saturday, April 15-16. The conference is free and open to the public. More information is available on the conference website: <http://uwm.edu/watercentriccities>.

## **Conference Organizers**

Patrice Petro, University of Wisconsin–Milwaukee

Jenny Kehl, University of Wisconsin–Milwaukee

## **Conference Speakers**

Dean Amhaus, The Water Council

Jean Cahan, University of Nebraska—Lincoln

B. Stephen Carpenter, II, Pennsylvania State University

Michael Carvan, University of Wisconsin–Milwaukee

Aimee Craft, University of Manitoba

Nancy Frank, University of Wisconsin–Milwaukee

Richard Grusin, University of Wisconsin–Milwaukee

Lane Hall, University of Wisconsin–Milwaukee

Matthew Howard, Alliance for Water Stewardship

Carolyn Johns, Ryerson University

Patrice McMahan, University of Nebraska—Lincoln

Oriol Miroso, University of Wisconsin–Milwaukee

Sara Mitchell, University of Iowa

Michael Nosonovsky, University of Wisconsin–Milwaukee

Raul Pacheco-Vega, Center for Economic Teaching & Research

Karen Sands, Milwaukee Metropolitan Sewerage District

Erick Shambarger, Office of Environmental Sustainability

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