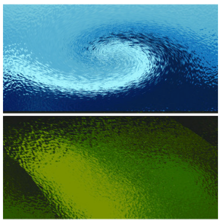
Transitional Waters Bulletin
TWB, Transit. Waters Bull. 9 (2015), n. 1, 11-19
ISSN 1825-229X, DOI 10.1285/i1825229Xv9n1p11
http://siba-ese.unisalento.it



RESEARCH ARTICLE

Water monitoring with hyperspectral techniques

T.M.P. Cattaneo[1], G. Bazar[2-3], A.A. Gowen[4], G.F. Greppi[5*], S. Mura[5], R. Tsenkova[2]

[1]Consiglio per la ricerca e la sperimentazione in Agricoltura, CRA-IAA, Milano, Italy.
[2]Biomeasurement Technol. Lab., Kobe University, Japan.
[3]Inst. Food and Agricult. Product Qualification, Kaposvar University, Hungary
[4]School of Biosystems Engineering, University College, Dublin, Ireland.
[5]DADU, Dipartimento di Architettura Design e Urbanistica, Palazzo del Pou Salit - Piazza Duomo 6 07041 Alghero (SS), Italy.

*Corresponding author: e-mail address: gfgreppi@uniss.it

Abstract

1 - The poor of the world depends directly on water and other natural resources for their livelihoods. Water resources must therefore be managed in a sustainable manner in order to maintain the economic, social and environmental functions and to contribute to the livelihoods of people.

2 - Advancements in sensor technologies and processing algorithms have resulted in technical capabilities that can record and identify Earth surface materials based on the interaction of electromagnetic energy with the molecular structure of the material being sensed.

3 - Non-destructive and operative methodologies (NIR and Raman) will be tested through field surveys and laboratory analysis using Aquaphotomics approach. This approach requires precise measuring and mapping capabilities at field level of key data at a sufficient level of accuracy depending on the availability of equipment that must be also operated at a cost-effective way.

Keywords: aquaphotomic, multivariate spectral analysis, pollution, waters

Introduction

Water is an invaluable resource for human health, food security, sustainable development and the environment. However, water resources are constantly under pressure from climate change, urbanization, pollution and overexploitation of freshwater resources (Mura *et al.,* 2014). Consequently, water security and biodiversity are at risk, the global demand for water is growing, and drought and floods cause deadly disasters (Wei *et al.,* 2011). Around 1500 substances have been listed as pollutants in freshwater ecosystems, and each of them occurs in the following types of freshwater pollutants: & alkalis; anions; domestic sewage and farm manures; detergents; gases (e.g. chlorine, ammonia); oil and oil dispersants; organic toxic wastes (e.g. formaldehyde, phenols); heat; heavy metals; food processing wastes; nutrients (especially phosphates, nitrates); pesticides; polychlorinated biphenyls; pathogens; radionuclides (Mura *et al.,* 2013, Kyle *et al.,* 2011). The range of pollutants encountered poses different challenges to freshwater ecosystems (Zaki and Hammam 2014).The persistent anthropogenic activity of the last centuries has lead to the continuous contamination of the environment by release of high levels of many chemical compounds

(Aardema *et al.,* 2002). In one study, the fish that live in a stream containing municipal effluents were found to contain concentrations of four antidepressants in their muscle tissue, liver and brain. Pharmaceuticals, among the emerging contaminants, are one of the most relevant groups of substances in aquatic ecosystems due to universal use, their chemico-physical properties and known mode of action in aquatic organisms at low concentrations (Heugens *et al.,* 2001; Ying and Kurunthachalam 2015). Once introduced in the environment, these compounds are assimilated by organisms, affecting their physiological condition. Most pollutants (pesticides, polyaromatic hydrocarbons (PAHs), antifouling agents, PCBs, dioxins and furans) and toxic elements (e.g. Hg, Cd, Pb and As), and other endocrine disrupting chemicals, pesticides and so on are persistent and accumulate in aquatic ecosystems, so that aquatic organisms are exposed during the whole life cycle and over generations (Ielmini *et al.,* 2014; Lajeunesse *et al.,* 2011 a,b). Spectroscopy has increasingly becoming a very important source of information in various fields, especially in biology. Water is the most substantial and widely distributed, but yet not well understood, component of biological systems. Its role is a complex subject which has received considerable attention over the years (Eric and Davies 1993); numerous papers in many scientific areas have been published on its properties, structure and functions (Facci, 2014; Szabo and Minamyer, 2014). Aquaphotomics provides an opportunity to start building up a "water vocabulary" and a suitable innovative tool for monitoring water-biosystems. Aquaphotomics is an "Omes and omics" concept, involving technologies, such as hyperspectral IR, NIR, Raman, and THz time-resolved spectroscopy to provide non-invasive and non-destructive analysis of aqueous systems (Mura *et al.,* 2012). Information on the absorbance bands can provide a distinctive knowledge of water vibrations and intrinsic interactions between water and other components of the aqueous system (Figure 1). By understanding the dynamics of the light-water interaction and its relation to biological function, aquaphotomics brings together the knowledge gained from other disciplines such as omics, genomics, proteomics, metabolomics, etc. that describe the individual elements of biological systems. This paper reports an update of recent research results obtained using the Aquaphotomics approach by the International scientific Community, and presented during the first Aquaphotomics seminar held in Brussels on October 14, 2014.

Methodological approach

Aquaphotomics aims at the collective characterization and quantification of water molecules having the same molecular vibrations that translate into structure, function, and dynamics of organisms or aqueous systems. Aquaphotomics is a new concept, introduced by Prof. Roumiana Tsenkova from Kobe University, Japan, (Tsenkova, 2006a) to describe rapid and comprehensive analysis of water-light interaction at each frequency of the electromagnetic spectrum as a potential source of information for better understanding of the biological world through the water and spectroscopy. Water, as a natural biological matrix containing only small molecules with strong potential for hydrogen bonding, changes its absorbance pattern when adapting to physical or chemical changes in biological systems or the environment (Segelstein, 1981). Therefore, its spectral behaviour allows the measurement of even subtle quantities or structural changes in other molecules in the aqueous system as well. Such techniques have become standard quality analysis tools in the food and

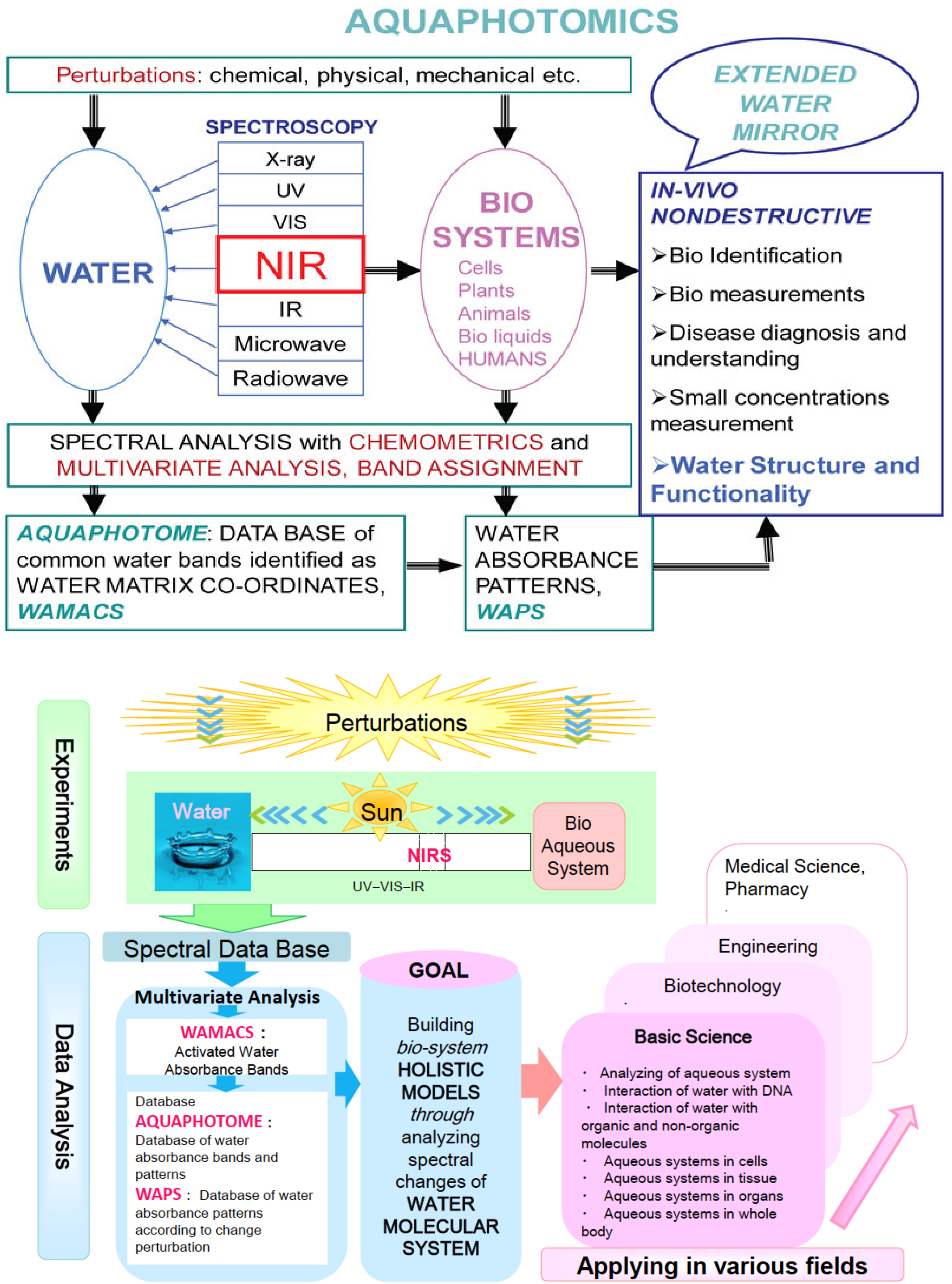


Figure 1. Aquaphotomics is an "Omes and omics" concept.

they are commonly implemented as process analytical technologies for continuous quality monitoring. Fundamental frequencies for molecular vibrations (e.g. stretch- ing, bending) occur in the MIR region while their overtones and combinations appear in the NIR spectral range. Absorption bands tend to overlap in the NIR, resulting in a broad spectral response; consequently, the NIR range contains less accessible molecule-specific information than does the MIR (Gowen *et al.,* 2013).

In a defined environment, each biomolecule has a unique water absorbance pattern described by the spectra of its solution. Activated Water Matrix Coordinates, (WAMACS) i.e. water absorbance bands in the NIR range, can therefore be used for its identification and concentration measurement. Vis/NIR spectral analysis at water absorbance bands allows non-invasive measurements of water structure and composition (Figure 2), (Tsenkova, 2006b). The absorbance pattern found by the absorbance at each WAMACS is called a water absorbance pattern (WAP) (Tsenkova, 2007). The database that contains all the respective WAPs of the same organism under various chemical, physical, mechanical, biological etc. perturbations is called the aquaphotome (Tsenkova, 2009). Uncovering details about WAMACS and building up the aquaphotome for each biological system is the subject of aquaphotomics and it will bring new knowledge about life and water (Figure 3).

VIS/NIR wavelength range (680-2500 nm) exhibits broad absorbance bands of water representing several absorbance peaks. Multivariate spectral analysis (Gowen *et al.,* 2013; Tsenkova, 2009) reveals that changes with the water matrix under perturbation reflect, like a mirror, the rest of the molecules surrounded by water. As a result, characteristic water absorbance patterns are used to measure very small concentrations of solutes and for disease diagnosis. Aquaphotomics has been developed using a deductive approach. It has two main goals: To expand knowledge about the interaction between water and electromagnetic radiation; knowing all possible bands and spectral regions (water matrix coordinates, WAMACS) where water interacts with light and, thus could be monitored. To use the water absorbance patterns, WAPS, based on WAMACS and related to water structure and functionalities in various systems, in order to deduct information about water/system peculiarities. Water quality monitoring is a complex multi-spatial and multi- temporal problem, extending from safety monitoring of drinking water to operational monitoring of waste waters. Standard methods for water quality analysis involve intensive sampling regimes and multi-step sample preparation, requiring manual inputs which prohibit their integration into continuous monitoring sys-tems. Consequently, there is currently a need for the development of low-cost, robust, reliable monitoring techniques that can be easily integrated into water flow systems (Gowen *et al.,* 2015).

Results and Discussion

A typical example of Aquagram for studying water and vapor is shown in Figure 3. Aquagram was devised to visualize WAPs. It displays normalized absorbance values using SNV (Standard Normal Variate) as data pre-treatment at specific absorbance bands on the axes originated from the centre of the graph. Absorbance values at the WAMACS are placed on the respective radial axes (Tsenkova, 2007; Segtnan *et al.,* 2001).

The first symposium on Aquaphotomics held in Brussels on October 14th 2014, pointed out the flexibility and the suitability of this scientific approach. Scientists coming from 12 countries (Austria, Belgium, Bulgaria, Czech Republic, Hungary, Ireland, Italy,

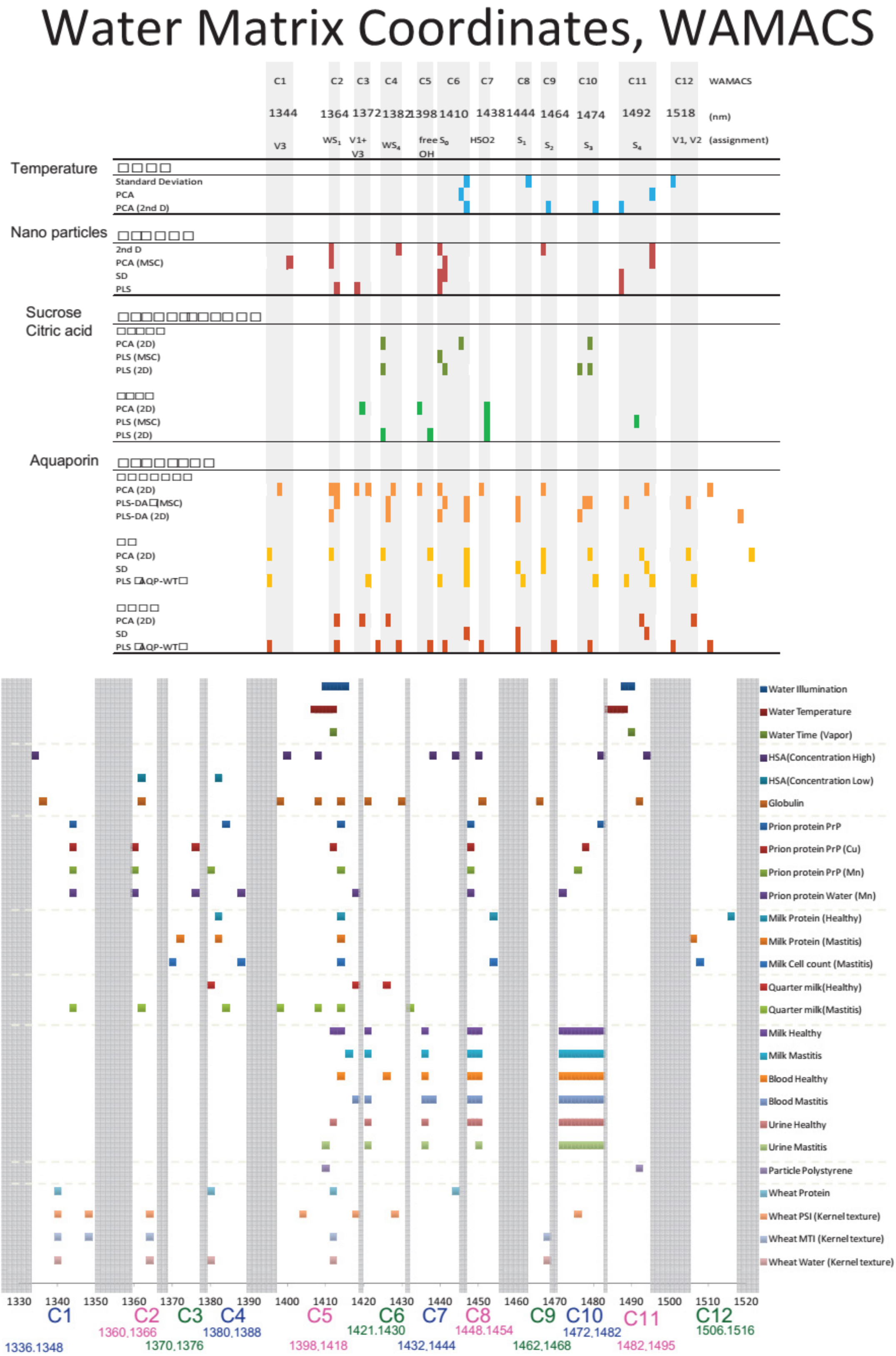


Figure 2. Activated Water Matrix Coordinates (WAMACS).

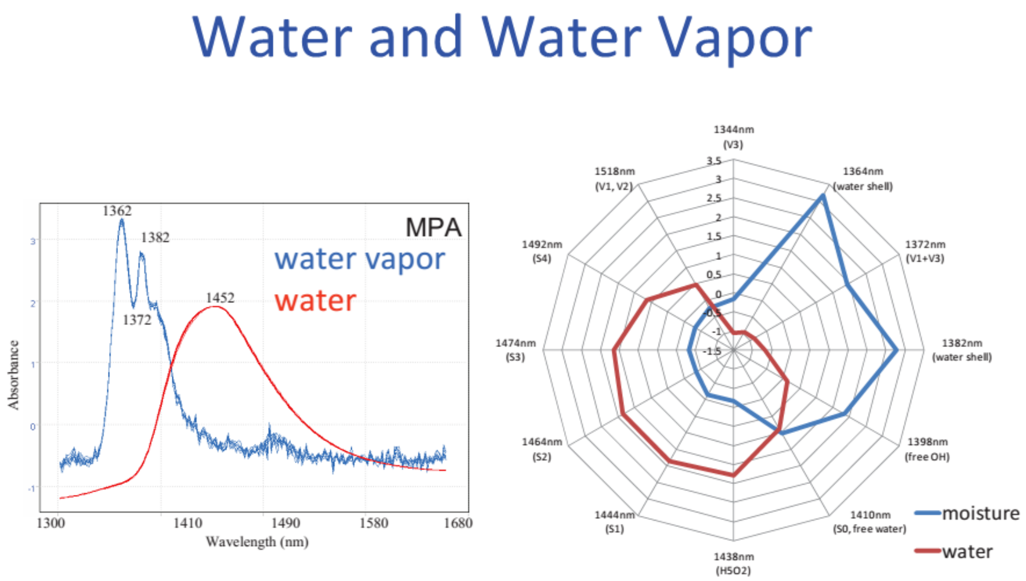


Figure 3. Activated Water Matrix Coordinates (WAMACS).

Japan, Netherlands, Norway, Serbia, Syria) exchanged their experiences showing robust evidences about its applicability in several fields (www.aquaphotomics.com; www.nirslab.org). One of them is measuring very low concentrations of solutes (>1000 ppm). Actually ions have no spectral features in NIR range, but NIR prediction of ions concentration in water is possible: ions alter water structure, so they can be indirectly detected using the interaction of water and NIR light (Sakudo *et al.,* 2006; Sakudo *et al.,* Heugens, *et al.,* 2001; Cattaneo *et al.,* 2011; Cocchi *et al.*, 2012). Other applications are related to water quality and functionality evaluation (Giangiacomo *et al.,* 2010), understanding functionality of microorganisms (Morita *et al.,* 2011; Remagni *et al.,* 2012) and water molecular changes related to amyloid formation (Chatani *et al.,* 2014), diagnosis of physiological conditions (Sakudo *et al.,* 2005; Sakudo *et al.,* 2006; Kinoshita *et al.,* 2012) etc., all based on the holistic approach using the information that water molecular system provides. Furthermore, Aquaphotomics has potential use in food science, mainly if coupled with new chemometrics tools such as NIR hyperspectral imaging (Gowen *et al.,* 2012; Gowen *et al.,* 2012a).

Conclusions

Water is perhaps the most studied material today; it has been studied with different tools and methods, but its behavior is still the subject of intensive scientific research. At a molecular level, water is not a homogeneous structure, but rather dynamic equilibrium among changing percentages of assemblages of different oligomers and polymer species. The structure and these assemblages or units themselves are dependent on temperature, pressure and composition. EXTENDED WATER MIRROR with near infrared light, NIR as WATER is a molecular NETWORK, NIR light can penetrate, get partially absorbed and bring information for the surrounding molecules making water a mirror on molecular level.

The Aquaphotomics approach was found to be highly informative when applied in various fields, such as medical, food and pharmaceutical. Using water-light interaction based methods we wanted to 'shed some light' on the water structure in a hope to see 'inside the water' and if it is possible to find some conclusions how different molecular structure of water gives different properties. Future work will involve dissemination of this knowledge and developing the entire "aquaphotome", i.e. collective characterization of all possible "windows" of electromagnetic spectrum where water molecular system could be observed. In the future, we expect to be able to explain how the water spectral pattern is related to food characteristics and functionalities, such as freshness. Overtone Vibrational Spectroscopy: a powerful tool for non- invasive water observation: immense information about water molecular conformations and respective function for understanding of the biological world. Another important future direction is to understand how water, as the matrix of life, changes with time and environmental changes like temperature, humidity, atmospheric pressure. We must also consider that the analytical approach, is inexpensive, non-destructive and requires no sample pretreatment. Recent advances in the field of optometric instruments, allow you to have portable instruments with reasonable costs.

References

Cattaneo TMP,. Vero S, Napoli E, Elia V 2011. Influence of Filtration Processes on Aqueous Nanostructures by NIR Spectroscopy. *Journal of Chemistry and Chemical Engineering* (5) 1046-1062.

Chatani E, Tsuchisaka Y, Masuda Y, Tsenkova R 2014. Water molecular system dynamics associated with amyloidogenic nucleation as revealed by real time near infrared spectroscopy and aquaphotomics. Collection 2014. PMID: 25013915 [PubMed] Free PMC Article.

Cocchi M, Li Vigni M, Vero S, Cattaneo TMP, Elia V 2011. Near infrared spectroscopy to explore water structure modification induced by filtration processes. In: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Cape Town, South Africa, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey; pp. 243-246.

Eric J, Davies D 1993. The use of vibrational spectroscopy in water analysis, Science of The Total Environment 135 (1–3): 145-152.

Facci P 2014. Life and the Water-Based Environment, In Micro and Nano Technologies. In: Facci, P., (Eds.), *Biomolecular Electronics*. William Andrew, Oxford, pp. 49-98.

Giangiacomo R, Marinoni L, Cattaneo TMP 2010. What's the Type of Water You Use? in: Proceedins of 14th International Conference on Near Infrared Spectroscopy, Bangkok, Thailand, Edited by S. Saranwong, S. Kasemsumran, W. Thanapase and P. Williams, pp. 827-830.

Gowen AA, Marini F, Tsuchisaka Y, De Luca S, Bevilacqua M, O'Donnell C, Downey G, Tsenkova R, 2015. On the feasibility of near infrared spectroscopy to detect contaminants in water using single salt solutions as model systems. *Talanta,* 131: 609-618.

Gowen AA, Amigo JM, Tsenkova R 2013. Characterisation of hydrogen bond perturbations in aqueous systems using aquaphotomics and multivariate curve resolution alternating least squares. *Analytica Chimica Acta,* 759:8-20.

Gowen AA, Amigo JM, Tsenkova R 2013. Characterisation of hydrogen bond perturbations in aqueous systems using aquaphotomics and multivariate curve resolution-alternating least squares. *Analytica Chimica Acta* 759 (8):8-20

Gowen AA, O'Sullivan C, O'Donnell CP 2012a. Terahertz time domain spectroscopy and imaging: Emerging techniques for food process monitoring and quality control. *Trends in Food Science & Technology,* 25(1): 40-46.

Gowen AA, Tsenkova R, Bruen M, O'Donnell C 2012b. Vibrational spectroscopy for water quality analysis: a review. *Critical Reviews in Environmental Science and Technology,* 42(23):2546-2573.

Heugens E, Hendriks JA, Dekker T, van Straalen NM, Admiraal W 2001. A Review of the effects of multiple stressors on aquatic organisms and analysis of uncertainty factors for use in Risk Assessment. *Critical Reviews in Toxicology,* 31 (3): 247-284.

Ielmini SE, Piredda G, Mura S, Greppi GF 2014. Protein biomarkers as indicator for water pollution in some lagoons of Sardinia (Italy). *Transitional Water Bulletin,* 1: 32-52.

Kinoshita K, Miyazaki M, Morita H, Vassileva M, Tang C, Li D, Ishikawa O, Kusunoki H, Tsenkova R 2012. Spectral pattern of urinary water as a biomarker of estrus in the giant panda. *Scientific Reports*, 2: 856.

Kyle E.M, Sheeba M, Thomas A, Bodour A 2011. Prioritizing research for trace pollutants and emerging contaminants in the freshwater environment. *Environmental Pollution,* 158 (12): 3462-3471.

Lajeunesse A, Gagnon C, Gagné F, Louis S, Čejka P, Sauvé S 2011a. Distribution of antidepressants and their metabolites in brook trout exposed to municipal wastewaters before and after ozone treatment - Evidence of biological effects. *Chemosphere*, 83(4): 564-71.

Lajeunesse A, Gagnon C, Gagné F, Louis S, Čejka P, Sauvé S. 2011b. Seasonal distribution of pharmaceuticals in marine water and sediment from a mediterranean coastal lagoon (SE Spain). *Environmental Research,* 138: 326-344.

Mi-Jung B, Young-Seuk P 2014. Biological early warning system based on the responses of aquatic organisms to disturbances: A review, *Science of The Total Environment*, 466–467: 635-649.

Morita H, Hasunuma T, Vassileva M, Tsenkova R, Kondo A. 2011. Near infrare spectroscopy as high-throughput technology for screening of xylose-fermenting recombinant Saccharomyces cerevisiae strains. *Analytical Chemistry,* 83(11):4023-9.

Mura S, Carta D, Roggero P, Cheli F, Greppi GF 2014. Nanotechnology and its applications in food and animal science. *Italian Journal of Food Science* 26(1): 92-102.

Mura S, Greppi GF, Marongiu ML, Roggero PP, Ravindranath SP, Mauer J, Schibeci N, Piccinini M, Innocenzi, P, Irudayara J 2012. FTIR nanobiosensors for Escherichia coli detection. *Beilstein Journal of Nanotechnology*, 3: 485-492.

Mura S, Greppi GF, Roggero PP, Musu E, Pittalis D, Carletti A, Ghiglieri G, Irudayaraj J 2013. Functionalized gold nanoparticles for the detection of nitrates in water. *International Journal of Environmental Science and Technology,* 12 (3): 1021-1028. DOI: 10.1007/s13762-013-0494-7

Remagni MC, Marinoni,L, Mora D, Carminati D, Cattaneo TMP 2012. The use of near infrared spectroscopy for monitoring milk-whey biotransformation processes using Lactobacillus plantarum. in: Proceedings of the 15th International Conference on Near Infrared Spectroscopy, Cape Town, South Africa, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey; pp. 439-443.

Sakudo A, Tsenkova R, Onozuka T, Morita K, Li S, Warachit J, Iwabu Y, Li G, Onodera T, Ikuta K 2005. A novel diagnostic method for human immunodeficiency virus type-1 in plasma by near-infrared spectroscopy. *Microbiology and Immunology,* 49(7):695-701.

Sakudo A, Tsenkova R, Tei K, Morita H, Ikuta K, Onodera T 2006 Ex vivo tissue discrimination by visible and near-infrared spectra with chemometrics. *The Journal of Veterinary Medical Science,* 68(12): 1375-8.

Sakudo A, Tsenkova R, Tei K, Onozuka T, Ikuta K, Yoshimura E, Onodera T 2006. Comparison of the vibration mode of metals in HNO3 by a partial least-squares regression analysis of near-infrared spectra. *Bioscience Biotechnology and Biochemistry*, 70(7):1578-83.

Sakudo A, Yoshimura E, Tsenkova R, Ikuta K, Onodera T 2007. Native state of metals in non-digested tissues by partial least squares regression analysis of visible an near-infrared spectra. *The Journal of Toxicological Sciences*, 32(2):135-41.

Segelstein D 1981. The Complex Refractive Index of Water. MSc Thesis, University of Missouri-Kansas City.

Segtnan VH, Šašic Š, Isaksson T, Ozaki Y 2001. Studies on the structure of water using two-dimensional near-infrared correlation spectroscopy and principal componen analysis. *Analytical Chemistry*, 73: 3153-3161.

Szabo J , Minamyer S 2014. Decontamination of biological agents from drinking water infrastructure: A literature review and summary. *Environment International*, 72: 124-128.

Tsenkova R 2006a. Aquaphotomics: exploring water–light interactions for a better understanding of the biological world. *NIR news*, 17(4):10-11.

Tsenkova R 2006b. Aquaphotomics: water absorbance pattern as a biological marker. *NIR news*, 17(7): 13-15.

Tsenkova R 2007. Aquaphotomics: water absorbance pattern as a biological marker for disease diagnosis and disease understanding. *NIR news,* 18(2): 14-16.

Tsenkova R 2009. Introduction: Aquaphotomics: dynamic spectroscopy of aqueous and biological systems describes peculiarities of water. *Journal of Near Infrared Spectroscopy*, 17(6): 303-313.

Wei S, Xiaodong Z, Zhen W, Xiaohui S, Jianxi H, Siquan Y, Sanchao L 2011. Analyzing disaster-forming environments and the spatial distribution of flood disasters and snow disasters that occurred in China from 1949 to 2000. *Mathematical and Computer Modelling* , 54 (3–4): 1069-1078,

Ying G, Kurunthachalam K 2015. Analytical Methods for the Measurement of Legacy and Emerging Persistent Organic Pollutants in Complex Sample Matrices, In: Eddy Y. Zeng, (Eds.), *Comprehensive Analytical Chemistry*, Elsevier, pp. 1-56.

