Modern Environmental Science and Engineering

Volume 2, Number 12, December 2016

Academic Star

Subscription Information:

Price: US$500/year (print)

Those who want to subscribe to our journal can contact: finance@academicstar.us.

Peer Review Policy:

Modern Environmental Science and Engineering (ISSN 2333-2581) is a refereed journal. All research articles in this journal undergo rigorous peer review, based on initial editor screening and anonymous refereeing by at least two anonymous referees. The review process usually takes 2-4 weeks. Papers are accepted for publication subject to no substantive, stylistic editing. The editor reserves the right to make any necessary changes in the papers, or request the author to do so, or reject the paper submitted.

Database Index:

Modern Environmental Science and Engineering (ISSN 2333-2581) is indexed by SSRN, CrossRef and Ulrich now.

Contact Information:

Manuscripts can be submitted to: mese@academicstar.us, environment@academicstar.us or cathy@academicstar.us. Constructions for Authors and Submission Online System are available at our website: http://www.academicstar.us/onlineupload.asp?shaction=show.

Address: 228 East 45th Street, Ground Floor, #CN00000267, New York, NY 10024
Tel: 347-566-2153, 347-230-6798 Fax: 646-619-4168, 347-426-1986
E-mail: mese@academicstar.us, environment@academicstar.us

Modern Environmental Science and Engineering

Volume 2, Number 12, December 2016

Contents

Technical Papers

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 765-768
Doi: 10.15341/mese(2333-2581)/12.02.2016/001
Academic Star Publishing Company, 2016
www.academicstar.us

Climate Warming and Long-Term Trends in Saskatchewan Hay Yield

Paul G. Jefferson

Western Beef Development Centre, P.O. Box 1150 Humboldt SK S0K 2A0, Canada

Abstract: Adaptation to climate warming is a key strategy for sustainable agriculture. Analysis of long-term trends in the provincial average hay yield in Saskatchewan from 1967 to 2011 has reported a decline since the 1970's and changing agronomic and economic variables were only partially effective in explaining the trend. In this paper, I examined the relationship between Global temperature difference and hay yield in Saskatchewan. Collinearity was determined by regression and principal component analysis. The beef cow number, fertilizer price, hay hectares, CO_2 concentration, and Global temperature difference are generally increasing with time in the dataset and exhibited collinearity with time. The residuals from the hay yield predicted from April, May and June (AMJ) precipitation were regressed on Global temperature difference. The significant ($P < 0.001$) relationship indicates that precipitation is becoming less effective (water use efficiency is declining) as global temperatures increase. Future hay crops must become better adapted to warming temperatures to reverse this trend.

Key words: climate change, precipitation use efficiency, adaptation, forage crops

1. Introduction

Analysis of long-term decline in Saskatchewan average hay yield has been associated with rising fertilizer prices, increasing beef cattle herd numbers and increasing hay hectares [1] or to changing crop rotations that reduced stored soil water for deep-rooted perennial forage crops [2]. As both reports noted, the problem of long-term trend analysis is that of collinearity of other variables that are also changing over time. Jefferson and Selles (2007) reported no long-term temperature trend in Saskatchewan spring (April, May and June) temperatures. However, climate change research has reported long-term global temperatures increasing over time [3]. The objective of this analysis was determine if global temperature change was associated with long-term change in Saskatchewan hay yield.

Corresponding author: Paul G. Jefferson, Ph.D., research areas/interests: forage agronomy. E-mail: pjefferson.wbdc@pami.ca.

2. Materials and Methods

The data base for this project was reported previously [1, 2]. Briefly, provincial average hay yield was obtained from a Saskatchewan Ministry of Agriculture database. Weather data from 16 weather stations representing the agricultural regions of Saskatchewan was obtained from the Environment Canada Historical Weather Database [4]. April, May, and June (AMJ) monthly precipitation, maximum temperature, mean temperature and minimum temperature by month was summed or averaged as appropriate to represent the growing conditions for the hay crop. Producers in Saskatchewan typically harvest one hay cutting per year and summer regrowth is either grazed or left to ensure good winter survival of the legume species. Data from the years 1967 to 2011 were included in this analysis which was 2 additional years compared to the previous study [2]. For more details on agronomic and economic variables examined in this

report, the reader is referred to Jefferson and Selles (2007) [1] and Jefferson and Larson (2014) [2].

Analysis was done with JMP Software (SAS Inc. Cary NC USA). Probability for significance in regression analysis was set at P = 0.05. Principal Component Analysis was used to examine the relationships among all the variables studied. Collinearity among variables was reported previously [1] and PCA was done to identify groups of variable that are associated with each other and to avoid collinearity in the analysis.

Global temperature difference data was obtained from the United Kingdom Meteorological Centre, Hadley England [3]. The data used global temperature data based on the change from the 1960 to 1990 baseline average global temperatures. The values in the global temperature difference data range from -0.212°C in 1974 to +0.509°C in 2005. There is a significant time-trend in the data ($R^2 = 0.82$, $P < 0.001$) over the period of this analysis (1967 to 2011).

3. Results and Discussion

The first and second principal components combined to explain 69% of the association among the variables. Year, Global temperature difference, Fertilizer Price Index, Beef Cow number, and Hay hectares were grouped together with positive values ranging from 0.296 to 0.389 for PC1 while Summerfallow hectares exhibited as different variable with -0.383 eigenvector value (Table 1). The values for hay yield (-0.526) and AMJ precipitation (-0.483) were grouped together contrasted with a temperature group of variables for April Maximum temperature (0.310), May Maximum temperature (0.538) and June Maximum temperature (0.233) in the second PC.

The PCA results also indicated that the collinearity in the dataset is associated with the variables that generally increasing over the time period, such as year, CO_2, Fertilizer Price Index, Beef cow numbers, and Hay hectares contrasted with the variable that is declining during the period, summerfallow hectares.

Table 1 Principal component analysis eigenvectors for component 1 and component 2.

Variable	PCA Component 1	PCA Component 2
Year	0.386	0.043
Summerfallow hectares	-0.383	-0.067
Hay yield kg ha^{-1}	-0.124	-0.526
Global temperature difference °C	0.361	0.112
April Maximum temperature °C	0.057	0.310
May Maximum temperature °C	-0.073	0.538
June Maximum temperature °C	-0.128	0.233
Fertilizer Price Index	0.364	0.038
AMJ precipitation mm	0.104	-0.483
Beef Cow number	0.296	-0.153
Hay hectares	0.385	-0.062
Atmospheric CO_2 ppm	0.389	0.023

The positive association between hay yield and precipitation and a negative association with temperature that was previously reported [1] was confirmed in the results of the second principal component.

As previously reported [1], there was a relationship between AMJ precipitation and Saskatchewan hay yield (Fig. 1a). While the previous report suggested a linear relationship, this analysis indicated a reciprocal of precipitation equation was the best fit to the expanded database. An examination of the data points suggested that years earlier in the data base (1967 to 1990) tended to appear above the regression and later years (1990 to 2011) tended to appear below the regression line. The residuals from the regression equation were regressed on the Global Temperature Difference variable (Fig. 1b). The linear regression was significant ($R^2 = 0.29$, $P < 0.001$) indicating that as global warming has occurred the residuals about the precipitation/hay yield equation tend to become more negative. In other words, the same precipitation early in the study period tended to produce more hay than later in the period. For example 89 mm of AMJ precipitation in 1969 was associated with 3113 kg ha^{-1} hay yield, but 89 mm in 2001 was associated with 1724 kg ha^{-1} hay

yield. In another example, 100 mm was associated with 3136 kg ha^{-1} in 1987 but 99 mm was associated with 2016 kg ha^{-1} in 2009. A stepwise regression analysis indicated that AMJ precipitation and Global temperature difference explained 54% of the variation in Saskatchewan hay yield (P = 0.10). As the global temperatures warm, less hay is produced per mm of precipitation in Saskatchewan. This supports the earlier report that precipitation use efficiency for Saskatchewan's hay crop has declined [2] although that report also linked the decline to changing crop rotations. Cannell et al. (2003) reported declining summer hay yields in the UK due to increasing summer temperatures [5].

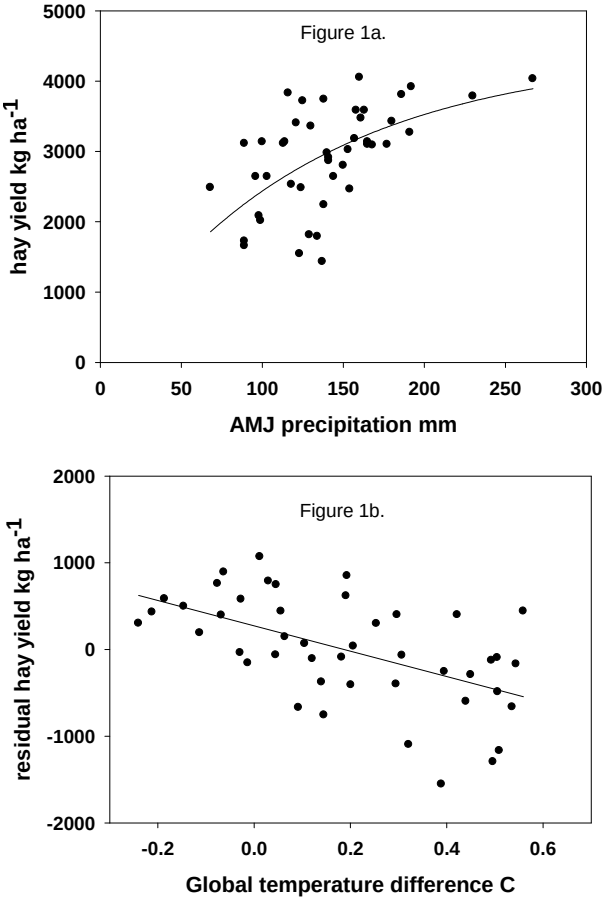


Fig. 1 Saskatchewan hay yield from 1967 to 2011 as correlated to annual spring (AMJ) precipitation with fitted reciprocal regression (Fig. 1a. R^2 = 0.24, P < 0.001) and residuals from that regression fitted to Global temperature difference with linear regression (Fig. 1 b. R^2 = 0.29, P < 0.001).

This new observation can be explained by the physiology of photosynthesis. Gas exchange between the atmosphere and plant tissues occurs through the leaf stomata with CO_2 entering the leaf to be absorbed by photosynthetic reactions in the mesophyll cells and H_2O vapour exiting the leaf. Water lost in this manner contributes to latent heat loss (cooling) of the leaf tissue. Optimum temperature for photosynthesis for C3 plants is 21°C. As air temperature increases, the amount of water lost to latent heat per g of carbon fixed increases. In water limited or semiarid environments, such as Saskatchewan, stomatal conductance to CO_2 and H_2O exchange is regulated to optimize both photosynthesis and water use efficiency. Water stress (drought) and high temperatures result in low stomatal conductance, low growth rate and reduced water loss. In Saskatchewan, perennial forage crops are primarily C3 plants so precipitation use efficiency will be reduced by higher temperatures.

Other crops, such as wheat, barley and canola, have reported yield increases during the same period of time [2]. In other words, these crops have demonstrated adaptation to increasing global temperatures while the hay crop has not. One difference between these crops is the rate of technology adoption. In wheat, for example, new cultivars are released from plant breeding programs continuously and are replaced by newer improved cultivars within a decade. In contrast, hay producers in Saskatchewan continue to use cultivars that were developed in the 1960s (Beaver and Algonquin alfalfas for example) because the cost of seed of new cultivars is higher and the perceived advantages are not apparent to producers. This suggests that slow technology adoption in hay crops may contribute to declining hay crop yield. Older forage crops (10 years or more since establishment) are common in Saskatchewan and may also contribute to poor precipitation use efficiency [6].

3. Conclusions and Implications

Hay yield and precipitation use efficiency of hay is

declining in Saskatchewan. The responsiveness of the hay crop to spring precipitation is declining and this appears to be associated with global temperature increases. This suggests that the Saskatchewan livestock industries will experience more hay shortages in the future as the global temperatures are predicted to continue to rise. Further research on precipitation use efficiency and high temperature adaptation in the breeding of new hay cultivars should be undertaken.

References

[1] P. G. Jefferson and F. Selles, The decline in hay yields: A Saskatchewan perspective, *Can. J. Plant Sci.* 87 (2007) 1075-1082.

[2] P. G. Jefferson and K. Larson, The relationship between Saskatchewan hay yield and changing cropping practices, *Can. J. Plant Sci.* 94 (2014) 1157-1160.

[3] Hadley Centre, Temperature anomaly (difference) from reference of period 1960 to 1990 in Centigrade, 2016, available online at: http://www.metoffice.gov.uk/hadobs/hadcrut4/data/current/time_series/HadCRUT.4.4.0.0.annual_ns_avg.tx.

[4] Environment Canada, Climate data online, July 2015, available online at: http://www.climate.weatheroffice.ec.gc.ca / climate Data/monthlydata_.html.

[5] M. G. R. Cannell, J. P. Palutikof and T. H. Sparks (Eds.), Indicators of climate change in the UK, DETR, 2003, available online at: http://www.ecn.uk/iccuk/.

[6] P. G. Jefferson and H. W. Cutforth, Sward age and weather effects on alfalfa yield at a semiarid location in southwestern Saskatchewan, *Can. J. Plant Sci.* 77 (1997) 595-599.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 769-774
Doi: 10.15341/mese(2333-2581)/12.02.2016/002
Academic Star Publishing Company, 2016
www.academicstar.us

Trees of Buenos Aires Changing the Appearance of the City

Maria Luisa Musso

School of Architecture, Design and Urbanism, University of Buenos Aires, Argentina

Abstract: The color of a city is not limited to the inherent color of the facades of their buildings. It must be considered the perceived color in all its complexity and all the elements which form the urban landscape, as buildings, equipment, trees. With regard to vegetation, important areas of Buenos Aires show modified the appearance by the trees in different seasons of the year. These sections refer only to the trees that produce changes in the appearance.

Key words: ornamental trees, trees and ecosystem, Charles Thays, visual appearance

1. Introduction

Buenos Aires is well known for the cultural value of its trees, part of the urban ecosystem intimately related to the inhabitants life. They grow for the ornamentation of our public spaces and for shade and shelter, differing in size, shape and color, but also by the texture of their trunks and branches, the color of its leaves and flowers According to recent studies, in the streets and squares of Buenos Aires there are more than 423.000 trees, equivalent to one tree every seven inhabitants, when the World Health Organization recommends one every three people in a city, in order to improve air quality.

Census data say there are 51.740 trees in parks and squares and 372.625 on sidewalks. The goal is to reach 100.00 in green spaces and 420,000 in sidewalks. Aesthetic benefits of trees relate to the possibility to see colors, structures, shapes and densities. Most of this aesthetic experience is subjective, and impacts on mental and emotional states of people [1]. Color is initially is a physical effect, but in sensitive people communicate immediately with the senses [2]. The visual appearance is that perception and, in many cases, knowledge through which an object is characterized or recognized as having attributes such as size, shape, color, texture, shine, translucency, opacity [3].

2. Some History

In the city of Buenos Aires, throughout history, tree growing data has been fragmentary from the colonial period. The first street of Buenos Aires was just a street with ombú trees, alongside the river. Until 1885 development in streets and squares was scarce and related to the initiatives of the inhabitants. In those days there were about 1,100 units in the city. During the presidency of Domingo Faustino Sarmiento (1868-1874) the trend of planting trees starts as a constant.

By the second half of the nineteenth century Buenos Aires incorporated the idea of green as a healthy city model under an organic notion of urbanism. “The city was considered as living organism breathing through the vegetation, promoting the quality of life of its inhabitants,” said Graciela Benito, curator of the Botanical Garden. This view

Corresponding author: Maria Luisa Musso, Architect, Consulting Professor, research areas/interests: colour research program. E-mail: colormlm@gmail.com.

prevailed in the planning of the Buenos Aires public spaces, where the landscape interventions were enhanced by the city's Directorate of Parks & Walkways. The architect Charles Thays and agronomist Benito Carrasco, between 1891 and 1918 drew up the guiding principles of this work, which not only looked the aesthetic, but also hygiene, leisure and population expansion. The French architect Jules Charles Thays arrived in Argentina in 1889, to design Sarmiento Park in Córdoba. He became captivated by the young country and decided to spend the rest of his life in Argentina. He was named the city's Director of Parks & Walkways in 1891. At the Competition to qualify in this position wrote: "Man, especially one that works, has need of distraction. There is something healthier, noble, true, that in contemplation of trees, beautiful flowers, when they are ordered with taste? The spirit then rests, and the appearance of beauty, purity, produces an immediate effect on the heart" [4].

This position gave him significant influence over the design of the city's open spaces, and his legacy is still strongly felt in the city's open spaces today. Thays worked most extensively in Buenos Aires precisely at a period where the city was growing extremely fast as a result of immigration, especially from Spain and Italy. He traveled around the country looking for species that would serve to decorate streets, parks and squares. From the north and northeast of Argentina brought several species as Pink Lapacho, Floss-Silk Tree, Tipa tree and Jacaranda, including some exotic ones.

3. Trees of Buenos Aires

Lapacho, *Tabebuia avellanedae,* or Pink Lapacho (Fig. 1), (*Family Bignoniaceae),* is a native tree of America, distributed from northern Mexico to northern Argentina, naturally found in the wild of Central to South American forests. It is widely planted as ornamental tree in public squares and boulevards due to its impressive and colorful appearance of it magenta flowers. Its corolla is pink or magenta, though exceptionally seen white. As soon initiated the spring in Buenos Aires, as an announcer of that, still without foliage, the tree spreads its thousands of pink flowers that dazzles with its extraordinary beauty. Flowering season is in early spring, in September, before the new leaves appear, but the ephemeral spectacle lasts only a few days. (ref. NCS S1040-R30B)*

Palo Borracho, (drunk sticks), Chorisia speciosa or Floss-Silk Tree (Fig. 2) (*Family Bombacacea*) is a deciduous tree native to Argentina and Brazil [5]. It grows fast when water is abundant, and sometimes reaches up to 25 meters in height, with broad crown, hemispheric. Its trunk is bottle-shaped, generally bulging in its lower third, measuring up to 2 meters in girth. It is studded with thick conical prickles. It bloom

Fig. 1 Lapacho, *Tabebuia avellanedae.*

Fig. 2 Palo Borracho, *Chorisia speciosa.*

in December, lasting to May or more, there are specimens that bloom early as October. The pink flowers, solitary, very showy, open before the leaves show and then remain for a long period. It is a very special tree. In autumn some keep their flowers and others already have their fruits, very big caplets in green color. Decorative species are in all its stages, for their flowers and for their fruits. When they open show the silky whitecotton, which surrounds the seeds. (ref.NCS S0540-R30B)*.

The Chorisia insignis is the variety with cream white flowers (ref. NCS S0505-Y)*

Paraiso, *Melia azedarach, (Family Meliaceae),* commonly called “paradise” in our country, is a deciduous tree, in the mahogany family. This tree, well known as Persian lilac, is native to India and Pakistan but is now grown in all the warmer parts of the world. It that can reach a height of 20 to 40 meters. Flowers are showy, fragrant, numerous on slender stalks, white to lilac in color. In winter, no leaves remain, just theses “China Berries” fruit, small, yellow, olive-like drupe, in cluster that are also very ornamental (Fig. 3) (ref. flower NCS S1020-R80B, fruit S1020-Y20R)*

Tipa tree, *Tipuana tipu* (Fig. 4) known as Rosewood, is a South American tree that can reach 40 meters high, providing shade and cooling effect in the summer heat. Notable for his size and elegance of the port, it is one of the most conspicuous and well known

Fig. 3 Paraiso, *Melia A. Fruits.*

Fig. 4 Tipa, *Tipuana tipu*.

trees of our flora. Very parasol like shaped and highly branched. It is appreciate also for its magnificent blooming yellow. They bloom only briefly in December when the yellow of the flowers mix with the green of the leaves, and upholster then with gold, the lawns, driveways and sidewalks. They are also called "the daughters of Thays" because before this landscape architect started to redesign the green areas in Buenos Aires, there were only 3 of them. He recommended the use of this tree in the city and now it is found everywhere. Tipa tree line many of the broad avenues where they grow in their normal development, spreading their branches, that meet in the middle, making us imagine within a green cathedral with high vaults. In winter, when they lose their leaves the strength of his bearing is shown (ref. NCS S1060-Y10R)*.

Jacaranda, *Jacaranda mimosifolia* (Fig. 5), a sub-tropical tree native to South America that has been widely planted because of its beautiful and long-lasting blue flowers in bloom all over the city. The flowers appear in spring and early summer, before the new leaves appear, and last for up to two months or more. There are more than 11.000 trees in the city and continue to be planting. The profuse flowering of these trees grace the plazas, parks, lines the major avenues. You can't avoid finding yourself with jacarandas wherever you may be." People are aware of the benefits they receive from this beautiful gift of colour" [6]. The foliage, green, is resembling a set of tenuous feathers. In winter, when it loses its leaves, fruits, large flat caps, decorate the branches (ref. NCS S1040-R70B)*.

Fresno Americano, White Ash, *Fraxinus Americana* (Fig. 6), is a tree from the temperate forests of North America, Asia and Europe. Tree providing a good and cool shade, reaches 15-20 m in height. The foliage, glossy green turns to bright yellow in autumn. The Fresno female have fruits provided with a wing, forming abundant clusters, that is green in spring and brown in autumn. The Fresno male is heavy, very green and robust tree. Unlike the female, not loading seeds

Fig. 5 Jacaranda, *Jacaranda m. and Jacarandas in the City*.

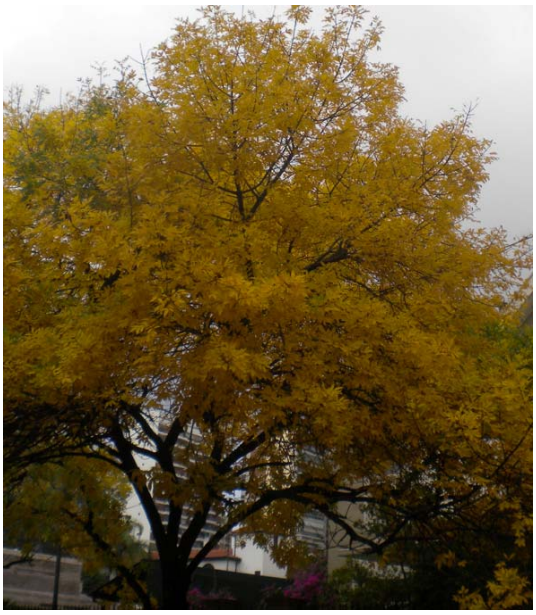


Fig. 6 Fresno Americano *Fraxinus A*.

and cup has twice the size. It is the species with the largest presence in the streets of the city, with more than 143.000 trees (ref. NCS S1060-10R)*.

Liquidambar, *Lyquidambar styraciflua* (Fig. 7) is a tree from Southern USA, Mexico and Guatemala, reaching 8 to 15 meters in height. Liquidambar comes from liquid and amber, alluding to the aromatic resin obtained from its bark. The leaves have five to seven lobules sharp; the upper side is bright dark green and the lower, clearer. In autumn they turn yellow to red and burgundy coloring the streets. The fruit is a spherical pendulum 2.5 to 4 cm in diameter and with numerous (20 to 50) capsules and each capsule is still open in the tree when the seeds are dispersed.

Platano, *Platanus acerifolia* (Fig. 8), it is considered a hybrid between two species: Platanus orientalis of Eurasian origin and Platanus occidentalis, of American origin. It is a deciduous tree that can reach above 40 meters high, providing a dense shade. There

Fig. 7 Liquidambar, *Lyquidambar s.*.

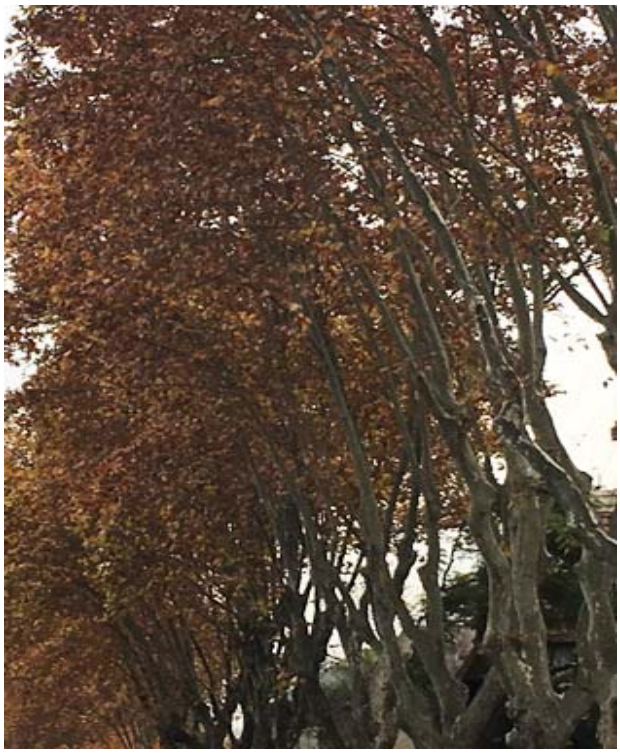


Fig. 8 Plátano, *Platanus*.

are about 35.00 trees in the streets. The crust is light grayish-brown color. Subsequently, very thin laminas come off leaving spots of lighter color. The large leaves are arranged alternately, green, lighter and pubescent underside fixing atmospheric dust particles, so that their action is significant decontaminant. The fruits are small and numerous, globular, hanging from long stalks and have a size close to 4 cm in diameter but the pollen from its fruits produces allergies. It bright green foliage turns yellowish and then to light brown in autumn and loses its leaves in winter.

4. Conclusions

Buenos Aires is a green City. It is very impressive how the color of flowers, leaves, trunks and its branches modifies the urban environment in different seasons of the year. There is a sense on the need to enjoy the color in nature that surrounds us, even in a big city like Buenos Aires.

The ornamental aspect is given by numerous features that together or separately, put the total value of ornamental plant, those who predominate in the

appreciation of this character are the colorful leaves and flowers and in some cases the trunks and in others the fruits.

Acknowledgements

*The NCS colours mentioned are only referential. The colour that we perceive is influenced by the intensity, angle and composition of the illumination, by the surrounding colours and by other factors that vary with the situation as for instance date and time. Colours perceived in complex situations depend on many other things than the physical radiation and the reflection qualities ofthe surface (Fridell Anter 1996/Gibson 1966). In the case of these flowers, differs also from flower to flower, from tree to tree of the same species, the site where they grow.

References

[1] L. Tyrväinen, S. Pauleit, K. Seeland and S. de Vries, *Benefits and Uses of Urban Forests and Trees, chapter 4 in Urban Forests and Trees,* Berlin. Springer, 2005.

[2] W. Kandinsky, *On the Spiritual in Art,* New York: Hilla Rebay Editor, published by the Solomon R. Guggenheim Foundation, 1946.

[3] D. Lozano, *La apariencia Visual y su medicion,* Buenos Aires, Editorial Dunken, 2015.

[4] S. Berjman, *Carlos Thays: sus escritos sobre jardines y paisajes*, Buenos Aires, 2002.

[5] C. Dalgas Frisch, *The Hummingbird Garden*, Sao Paulo, 1995.

[6] I. Messore, *Haciendo verde Buenos Aires*, El libro verde, Buenos Aires, Editors l C.Conte-706114, 2011.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 775-783
Doi: 10.15341/mese(2333-2581)/12.02.2016/003
Academic Star Publishing Company, 2016
www.academicstar.us

Concentration Retention and Enrichment of Ammonia Bicarbonate Draw Solution in Forward Osmosis Desalination

Bikasha Chandra Panda[1], Morgan Harry[2], and Ashok Kumar Ghosh[3]

1. Department of Civil Engineering, IGIT Sarang, Dhenkanal-759146, Odisha, India

2. Department of Chemical Engineering, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

3. Department of Mechanical Engineering, New Mexico Institute of Mining and Technology, Socorro, NM 87801, USA

Abstract: Following the presentation of the novel ammonia-carbon dioxide forward osmosis (FO) desalination method in 2005, ammonium bicarbonate has been used frequently for the preparation of draw solution. However, the ammonium bicarbonate (NH_4HCO_3) salt decomposes at higher temperatures and retains less concentration than the solute added for desired concentration. In this study, the concentration retention properties of NH_4HCO_3 draw solution, in relation to temperature, time and desired concentration have been investigated. In order to achieve the desired concentration, the solution was enriched either with additional amount of NH_4HCO_3 or ammonium hydroxide (NH_4OH) solution. The results revealed that NH_4OH is the good candidate to be added to the solution to get the targeted concentration.

Key words: desalination, forward osmosis, draw solution, ammonium bicarbonate, concentration retention, enrichment

1. Introduction

The growing global shortage of water and increasing demands for freshwater have led to a rising interest in desalination to produce water for both industrial and domestic usage. Currently, desalination plants based on thermal distillation and reverse osmosis, consume huge amounts energy. As a result, there has been always an interest in less-energy intensive approaches.

In recent times, forward osmosis (FO) process has been developed as a possible option for desalination, with the prospective for much lower energy consumption. In FO desalination method, an osmotic pressure gradient is created by a highly concentrated solution (Draw Solution) to pull water across a semi-permeable membrane from a feed water of lower salt concentration. As an osmotic pressure generator, draw solution plays the key role on the realization of forward osmosis.

Selection of draw solution has been an important aspect of past researchers. There are several reports on FO desalination which have mainly focused on attaining appropriate draw solutions using different type of chemicals that are either easily removable or consumable. An overview of these previous efforts is presented in Table 1 [1-16]. As per observation, ammonium bicarbonate (NH_4HCO_3) has been used frequently as draw solute after presentation of ammonia-carbon dioxide FO desalination method by McCutcheon et al. [9] in 2005. They have discussed ideal draw solution characteristics as well as have demonstrated that these criteria are satisfied by using ammonium bicarbonate draw solution. The concentrated draw solution was made by dissolving NH_4HCO_3 in deionized water. One main reason for

Corresponding author: Bikasha Chandra Panda, Ph.D., research areas/interests: environmental engineering, desalination, forward osmosis. E-mail: bikashapanda@yahoo.com.

using NH_4HCO_3 was the ease of separation of the fresh water from the draw solution. They performed FO experiments using 6M NH_4HCO_3 draw solution at 50°C for one hour. However, Gokel [17] reported that NH_4HCO_3 starts to decompose into ammonia, carbon dioxide, and water at 35°C, while complete decomposition is achieved above 60°C. The decomposition process causes ammonia and carbon dioxide gases to escape from the solution. As a result, the salt solution retains lesser solution concentration than what is intended. Also, Trypuc and Kielkowska [18] stated that NH_4HCO_3 salt is chemically unstable and decomposes at higher temperatures under atmospheric pressure. Considering that fact, they carried out investigations under required pressure conditions to prevent decomposition process. According to Speight [19], solubility of NH_4HCO_3 per 100 gram of water is 36.6 and 59.2 g at 40 and 60°C, respectively. On the other hand, Ng. et al. [11] found that NH_4HCO_3 was fully insoluble, when 36.6 g (4.064 M) of NH_4HCO_3 was dissolved in 100 gram of water even at 50°C. In addition, they observed gas bubbles releasing from the solution, which was an indication of NH_4HCO_3 decomposition. Due to these constraints, they conducted most of the experiments at 30 or 50°C with a draw solution concentration of 3M. No observed decomposition was found, in experiments conducted at 30°C. It was not possible for them, to produce 6 M of $NH4HCO_3$ draw solution at 50°C due to decomposition trouble. McCutcheon et al. [12] have made draw solution of desired concentration by mixing ammonium bicarbonate (NH_4HCO_3) and ammonium hydroxide (NH_4OH) with deionized water at proper proportions. They used higher ammonia to carbon dioxide molar ratios ranging from 1.2 for 1.1 M draw solution to 1.4 for 6M draw solution. During the FO tests, the draw solution temperature was held at 50°C. Asemsro [15] reported that additional amount of $NH4HCO_3$ salts above the calculated amount were needed to retain the solution concentration at 6 M. The experiments were conducted in FO mode at 50°C for one hour. Sarpong [16] found that lesser molar concentration of ammonium salt was retained than the desired molar amount that was mixed at the start of preparing the draw solution. In the investigation for recapture of ammonia carbon dioxide gases, molar concentration of 1 to 3 M of $NH4HCO_3$ solution were tested at 50 to 70°C for 1 hour to 2 hours.

Table 1 Overview of draw solutions used by past investigators with separation strategy.

Year	Ref.	Draw solution	Separation strategy adopted or assumed
1965	01	SO_2	Heating or stripping
1965	02	Alcohols, SO_2	Standard means
1972	03	Al_2SO_4	Add $Ca(OH)_2$
1975	04	Glucose	Ingestion purpose
1976	05	Glucose & Fructose	Ingestion purpose
1989	06	Fructose	Ingestion purpose
1992	07	Glucose	Low pressure RO
2002	08	KNO_3/SO_2	Precip. by cooling
2005	09	NH_4HCO_3	Moderate heating
2005	10	NaCl	Osmotic distillation
2006	11	NH_4HCO_3 ,Glucose, Fructose	Distillation/ingestion
2006	12	NH_4HCO_3, NH_4OH	Moderate heating
2008	13	Glucose Sucrose	Ingestion purpose
2009	14	NaCl, $MgCl_2$, NH_4HCO_3	RO or distillation
2009	15	NH_4HCO_3	Distillation
2010	16	NH_4HCO_3	Distillation

While many of these efforts contribute to the use of ammonium bicarbonate draw solution in FO experiments and share discussions on the observed solubility and decomposition problems, no work was found addressing in detail the concentration retention ability of the solution at different temperatures and its enrichment aspects to achieve the desired concentration. The purpose of this paper is to examine and disseminate the issues involved in preparing $NH4HCO_3$ draw solution. The solubility temperature and the temperature at the beginning of decomposition were reported over a wide range of molarities (1 M to 6 M). Concentrations of solution that were retained at solubility temperature sand at specific higher temperatures were presented. Also, loss of concentration in relation to time was investigated. Enrichment schemes like addition of excess $NH4HCO_3$ salt or NH_4OH solution were tested to achieve desired concentration level.

2. Experimental Investigation

2.1 Materials& Instruments

The following chemicals were used:

- Ammonium Bicarbonate: Fisher Scientific certified powder, M.W. 79.06.
- Sodium Chloride: Fisher Scientific certified crystalline, M.W. 58.44.
- Ammonium Hydroxide: Fisher Scientific certified, 14.8N, M.W. 35.05.
- Deionized (DI) Water (produced in a Millipore deionizing unit)

The following apparatuses and instruments were used for preparation of the required solutions and for measuring the required properties.

1) Kimax Kimble laboratory glassware assortment.
2) Biomega Hot Plate Magnetic Stirrer with stir bars.
3) Ohaus PA3102 Pioneer Precision Balance.
4) Fisher Scientific Thermocouple.
5) Oakton CON 610 waterproof TDS meter.
6) Precision System Inc. 5002 OSMETTE A™ Automatic High Sensitivity Osmometer.

2.2 Test Procedure

A total of seven batches of experiments were conducted for the investigation. First batch of $NH4HCO_3$ solution, staring from 1M to 6M desired concentrations were prepared to study the concentration retention abilities at solubility temperature and at 45, 50, 55 and 60°C respectively. The second batch of solution was prepared in terms of molalities, so as to observe the variability if any with that prepared in terms of molarities. The next three batches were devoted to examine the concentration retention abilities after keeping the solution for 30, 60, 90 and 120 minutes under constant temperature. The remaining two batches were assigned for concentration enrichment studies. The existing room temperature as well as the DI water temperature was measured previous to preparing any solution. Instruments like TDS meter and Osmometer were calibrated with standard solutions (supplied with kit). Sodium Chloride (NaCl) solution, which is more stable, was prepared in specific concentrations to validate these instruments. It was to make sure that these instruments were confirming the specific concentration of NaCl within ±99.9%, for the amount of solute that was added. To prepare the $NH4HCO_3$ solution of particular molarity (M) or molality (m), calculated quantity of salt was weighed according to the molecular weight. Ammonia bicarbonate solutions were prepared from 1M through 6M for concentration retention evaluation. The salt was kept inside the 2000 ml flask and the flask was placed on the hot plate magnetic stirrer. Magnetic stir bar was put inside the flask. If the concentration of solution was to be measured in terms of molarity, then DI water was poured in to the flask until total volume of solution became one liter. Otherwise, one kilogram of DI water was added for measuring concentration of solution in terms of molality. The hot plate magnetic stirrer was switched on to prepare the solution. Time was noted as zero at this instant. Endothermic down

temperature was noted three minutes after mixing the salt with DI water. Temperature and the time were noted down following the observation of gas bubbles releasing continuously from the solution. That instant was interpreted as the beginning of decomposition. The solution was said to be prepared, when it was appeared clear and transparent without any visible particles. Time and temperature were noted at the point of solution formation and samples were collected for concentration measurements. The prepared solutions were further heated and samples were collected each at 45, 50, 55 and 60°C for determining the concentration retention. Solutions were prepared separately to collect samples each at 50, 55 and 60°C after keeping it under constant temperature for 30, 60, 90 and 120 minutes. These data were useful to evaluate loss of concentration with time. For evaluation of the enriching efforts to achieve the desired concentration, two schemes were tried. In first scheme, additional amount by 0.5M of $NH4HCO_3$ salt was mixed to each solution of desired concentration from 1M through 6M. Ammonium hydroxide (NH_4OH) was added to $NH4HCO_3$ salt to make a composite solution in the second scheme. For composite salt solutions, samples were prepared from 1m through 6mand were collected only for Osmette, i.e., molality measurements.

2.4 Test Measurements

The temperature was measured using thermocouples to an accuracy of ±0.1°C. Temperature was controlled within ±1°C, when it was required to keep the solution at constant temperature for specific time. Oakton CON 610 TDS meter was used to measure total dissolve solids (TDS) of the solution in terms of ppm. Previous to any measurement, the instrument was calibrated daily with standard solution available with the meter kit. The osmolality of each solution was measured using a 5002OSMETTE A™ Automatic High Sensitivity Osmometer (Precision System Inc). The Osmometer determines the total osmolality of an aqueous solution by performing a comparative measurement of the freezing point of pure water and that of the solution being tested. A solution containing 1 Osmole (1000 m Osm) of dissolved solute per kg of water lowers the freezing point of water by 1.858°C [20]. In practice, however, the osmometer reads directly in mosm/kg H_2O by converting the thermistor readings by direct comparison with readings obtained using standard aqueous salt solutions of known osmolality. For example, 0.5 molality i.e., 0.5 gram mole of NaCl (osmotic coefficient of 0.93) salt in 1 kg of DI water will show a reading of 930 m Osm/kg H_2O in the Osmometer [20]. Similarly, 1 molality of $NH4HCO_3$ with a osmotic coefficient of 0.98 [21] will show a reading of 1960 m Osm/kg H_2O. The instrument was calibrated with standard solution, prior to any measurements. The Osmometer has a reading range of 0-3000 m Osm/kg H_2O. In view of the fact, each solution was diluted to same dilution factor, i.e., 10 so as to keep uniformity of test results.

3. Results and Discussions

3.1 Solubility of $NH4HCO_3$

$NH4HCO_3$ solutions with molarities starting from 1M to 6M were prepared. Immediately after mixing the salt with DI water, the temperature went down in the process, indicating an endothermic reaction. Only magnetic stirrer was switched on to prepare clear solution up to 2M without use of hot plate. The solution preparation process inventory for each molar concentration is presented in Table 2. The solubility temperature increases with increase in desired molar concentration. For 6M solution, solubility temperature was more than 50°C. The difference between existing DI water temperature and that of endothermic down temperature are reported inside bracket in Table 2. As the desired solution concentration increased, the temperature difference also increased from 5.2°C for 1M to 9.9°C for 6M. The endothermic effect was more as more quantities of solutes were mixed to make same volume of solution. Gas bubbles, i.e., decomposition of $NH4HCO_3$ was not observed for solutions of desired

concentration up to 3 M. Decomposition started around 35°C for solutions of 4 M and above.

3.2 Concentration Retention of $NH4HCO_3$ at Solubility Temperature

NH_4HCO_3 solutions prepared in provisions of molarities (1 M to 6 M) and molalities (1 m to 6 m) were tested for concentration retention measurements using TDS meter as well as Osmometer respectively. The measurements were taken immediately after the solution formation. The readings were multiplied with the dilution factor to evaluate real concentration of solution. The real TDS values in ppm were divided by the molecular weight (expressed in milligram) 79060 of $NH4HCO_3$ to convert to the molar values. Similarly, Osmometer values in mOsm are divided by 1960 to convert to the molal values. The concentration retention ability of NH_4HCO_3 are presented in Table 3 and Fig. 1. It was observed that desired solution concentration was never achieved for any molarity or molality values. Even if there was no visual decomposition for 3 M (3 m) or less, the retained concentration was less than the target. The percentage of retained concentration decreased with increase in desired solution concentration. Also, the percentage of retained concentration was nearly same for solutions, whether prepared in terms of molalities or molarities.

Table 2 One liter $NH4HCO_3$ solutions preparation inventory.

Desired solution conc. in Molarity	Existing Room Temp. in °C	Existing DI Water Temp. in °C	Endothermic down Temp. in °C	Bubble Point Temp. in °C	Solution Temp. in °C
1 M	17.3	14.9	9.7 (5.2)	Not observed	12.1
2 M	18.8	16.7	11.3 (5.4)	Not observed	16.3
3 M	16.6	13.7	6.4 (7.3)	Not observed	30.2
4 M	17.1	14.9	6.5 (8.4)	35.6	41.6
5 M	16.2	14.4	5.3 (9.1)	35.3	47.1
6 M	18.9	18.2	8.3 (9.9)	34.6	52.8

Table 3 Concentration retention ability of NH_4HCO_3 solution at solubility temperature.

Desired solution concentration in molarity (molality)	Concentration retained in molarity	Concentration retained in molality	% of desired molarity retained	% of desired molality retained
1 M (1 m)	0.938	0.952	93.80	95.20
2 M (2 m)	1.803	1.828	90.15	91.40
3 M (3 m)	2.592	2.604	86.40	86.83
4 M (4 m)	3.232	3.230	80.82	80.75
5 M (5 m)	3.720	3.797	74.40	75.94
6 M (6 m)	4.164	4.197	69.41	69.95

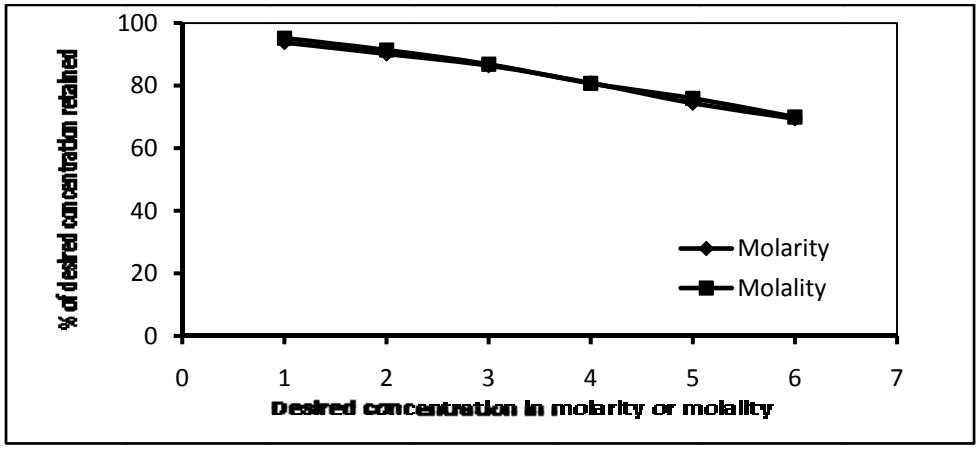


Fig. 1 Concentration retention ability of NH_4HCO_3 at solubility temperature.

3.3 Concentration Retention of NH_4HCO_3 at Higher Temperatures

The solutions prepared in terms of molarities were further heated to collect samples for determining the concentration retention with variation of temperature. Samples were collected at 45, 50, 55 and 60°C for solutions up to 4 M. For 5 M and 6 M solution, samples were obtained at 50, 55 and 60°C, and at 55 and 60°C respectively. The results are illustrated in Fig. 2. As per observation, for any molar value, the retention of concentration decreased with increase in temperature of solution due to decomposition. Another interesting finding was that at a particular temperature, the percentage of retention was nearly constant for each concentration and was independent of molarity of solution.

3.4 Concentration Retention of NH4HCO$_3$ with Time

As discussed in introduction section, FO tests are usually conducted at 50 to 55°C and for one to two hours. So, it was desired to test concentration retention with varying times from 30 minutes through 120 minutes at constant temperature. These solutions were prepared separately in terms of molarities. The results are presented in Fig. 3 through Fig. 5. At a particular temperature and for any molar value, the concentration retention decreased with increase in retention time of solution due to release of volatile gases to atmosphere. Also, the percentage of retention was nearly constant for each concentration of solution.

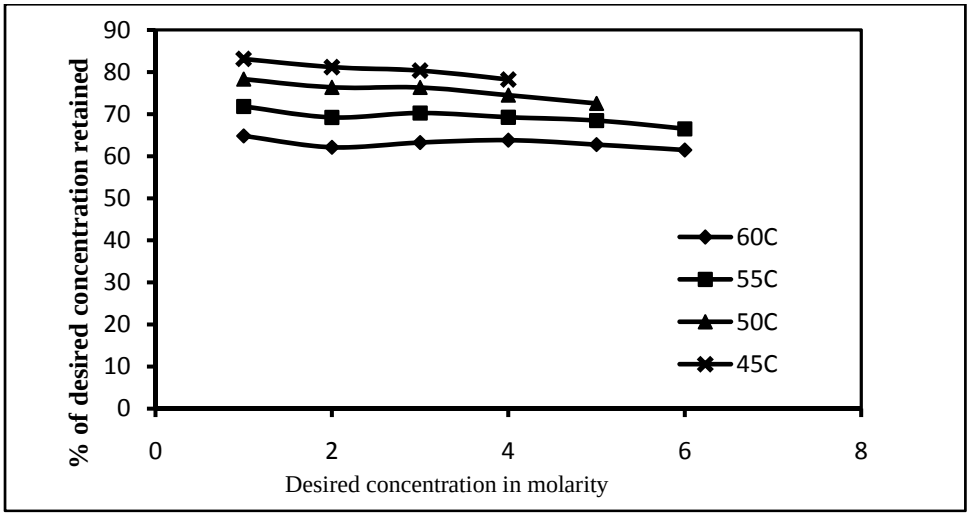


Fig. 2 Concentration retention ability of NH_4HCO_3 at higher temperatures.

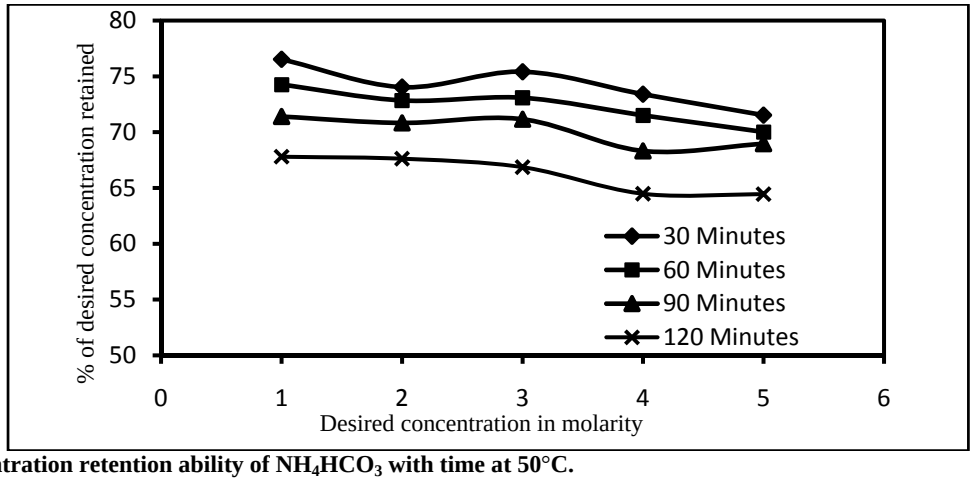


Fig. 3 Concentration retention ability of NH_4HCO_3 with time at 50°C.

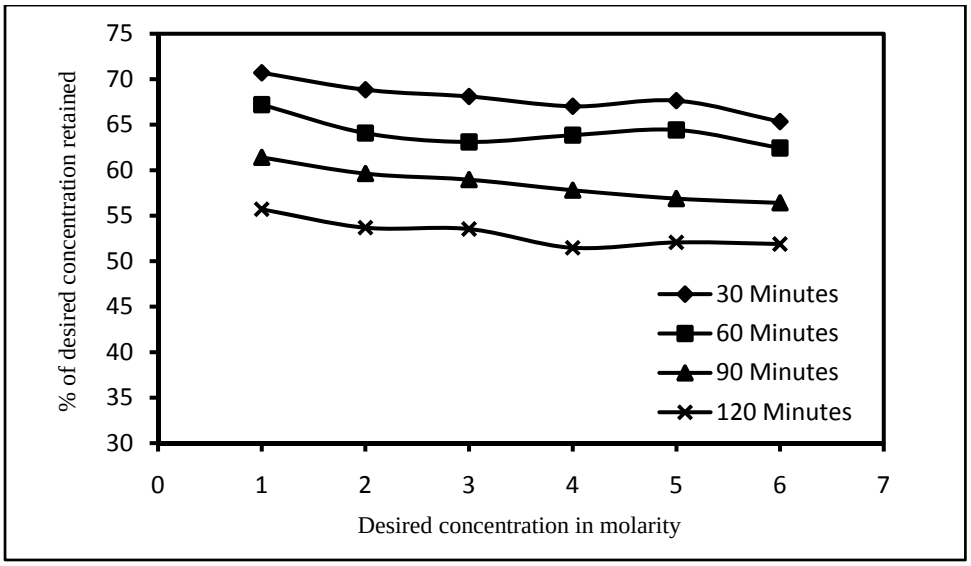


Fig. 4 Concentration retention ability of NH_4HCO_3 with time at 55°C.

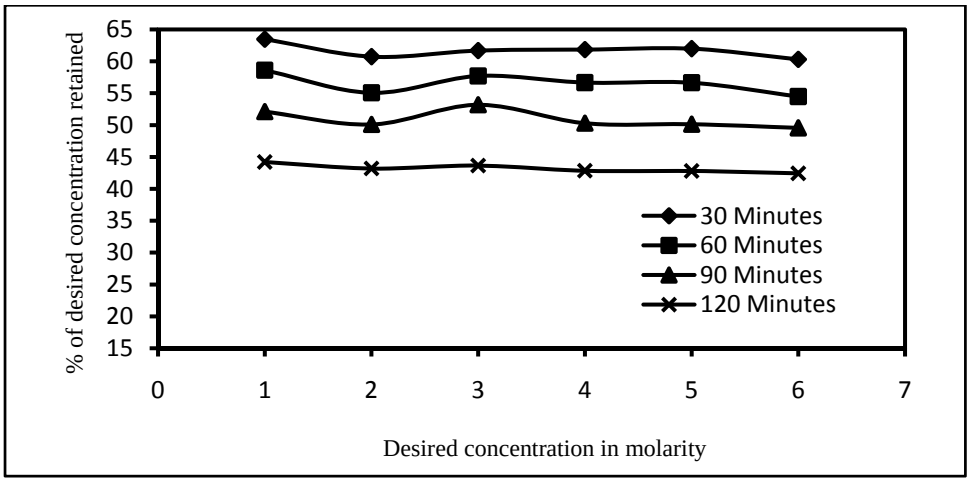


Fig. 5 Concentration retention ability of NH_4HCO_3 with time at 60°C.

3.5 Concentration Enrichment with Additional Amount of NH4HCO3

To get the desired solution concentration, trial was made to add extra amount of solute to the solution. For each desired molar concentrations up to 5 M, in addition to the calculated quantities, extra amount of solute by 0.5 M was added to DI water. Often, FO tests are conducted using a 6 M draw solution. To achieve the target concentration of 6 M, additional amount of solute by 0.5 M was added incrementally up to 8 M for each solution preparation. The results obtained are presented in Table 4. The samples were collected at solubility temperature. Target concentrations have been achieved up to 2 M solution. The desired solution concentration was never achieved for 6 M even after adding the solute in increments by 0.5 M up to 8 M.

3.6 Concentration Enrichment of $NH4HCO_3$ Solution with Addition of NH_4OH.

To achieve the target molar concentration, ammonium hydroxide (NH_4OH) was added at the start of solution preparation. To keep the track of the amount of ammonium hydroxide, the molar ratio between ammonia and carbon dioxide was recorded for each solution preparation. Solutions were prepared in terms of molality and measurements were taken in the Osmometer. NH_4OH was added with incremental

molar ratio, until and when the desired concentration was achieved or exceeded. The results obtained are presented in Table 5. Unlike NH_4HCO_3, addition of NH_4OH caused exothermic reaction. The endothermic down from DI water temperature was almost regained by addition of NH_4OH solution. Almost in every case desired solution concentration was achieved for any molality values up to 6m. The ammonia to carbon dioxide molar ratios used in preparing the solution were ranged from 1.120 for 1m desired concentration to 1.884 for 6m.

Table 4 Concentration enrichment efforts with additional amount of NH_4HCO_3 by 0.5 M.

Desired solution concentration in molarity	Equivalent total concentration after solute addition by 0.5 M in molarity	Concentration retained in molarity	% of desired molarity retained
1 M	1.5	1.312	131.20
2 M	2.5	2.139	106.95
3 M	3.5	2.913	97.10
4 M	4.5	3.586	89.65
5 M	5.5	4.092	81.84
6 M	6.5	4.647	77.45
6 M	7.0	4.824	80.40
6 M	7.5	4.966	82.78
6 M	8.0	5.202	86.70

Table 5 Concentration enrichment of NH_4HCO_3 solution with addition of NH_4OH

Desired solution concentration in molality	Ammonia to carbon dioxide molar ratio kept during preparation	Concentration retained in molality at solubility	% of desired molality retained
1 m	1.120	1.102	110.200
2 m	1.203	2.068	103.400
3 m	1.326	3.046	101.533
4 m	1.479	4.132	103.300
5 m	1.652	5.024	100.480
6 m	1.884	6.102	101.700

4. Conclusion

The data presented in this study demonstrate that ammonium bicarbonate draw solution is unstable and decomposes with increasing delay time and temperature. The desired concentration of solution cannot be achieved by mixing only ammonium bicarbonate solute with DI water. Ammonia bicarbonate and ammonium hydroxide shall be mixed at proper proportions to produce a solution of desired concentration.

Acknowledgements

The paper is a part of research project “Desalination of Produced water using membrane technology for Lea County” under the grant DE-NT0005227-06-1-0951 carried out at New Mexico Tech.

References

[1] G. W. Bathchelder, Process for the demineralization of water, *US Patent* 3,171,799 (1965).

[2] D. N. Glew, Process for liquid recovery and solution concentration, *US Patent* 3,216,930(1965).

[3] B. S. Frank, Desalination of sea water, *US Patent* 3,670,897 (1972).

[4] R. E. Kravath and J. A. Davis, Desalination of seawater by direct osmosis, *Desalination* 16 (1975) 151-155.

[5] J. O. Kessler and C. D. Moody, Drinking-water from sea-water by forward osmosis, *Desalination* 118 (1976) 297-306.

[6] K. Stache, Apparatus for transforming seawater, brackish water, polluted water or the like into a nutrious drink by means of osmosis, *US Patent* 4,879,030 (1989).

[7] J. Yaeli, Method and apparatus for processing liquid solutions of suspensions particularly useful in the desalination of saline water, *US Patent* 5,098,575 (1992).

[8] R. L. McGinnis, Osmotic desalination process, *US Patent* 6,391,205 B1, 2002.

[9] J. R. McCutcheon, R. L. McGinnis and M. Elimelech, A novel ammonia-carbon dioxide forward osmosis desalination process, *Desalination* 174 (2005) 1–11.

[10] T. Y. Cath, S. Gormly, E. G. Beaudry, M. T. Flynn, V. D. Adams and A. E. Childress, Membrane contactor processes for wastewater reclamation in space, Part I. Direct osmotic concentration as pretreatment for reverse osmosis, *J. Membr. Sci.* 257 (2005) 85-98.

[11] H. Y. Ng, W. Tang and W. Wong, Performance of forward (direct) osmosis process: Membrane structure and transport phenomenon, *Environmental Science & Technology* 40 (2006) (7) 2408-2413.

[12] J. R. McCutcheon, R. L. McGinnis and M. Elimelech, Desalination by ammonia-carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance, *J. Membr. Sci.* 278 (2006) 114-123.

[13] M. Wallace, Z. Cui and N. P. Hankins, A Thermodynamic benchmark for assessing an emergency drinking water device based on forward osmosis, *Desalination* 227 (2008) 34-45.

[14] N. T. Hancock and T. Y. Cath, Solute coupled diffusion in osmotically driven membrane process, *Environmental Science & Technology* 43 (2009) (17) 6769-6775.

[15] D. H. Asemsro, A forward osmosis based treatment process for high TDS oilfield produced water, MS Thesis, New Mexico Institute of Mining and Technology, Socorro, NM, 2009.

[16] G. Sarpong, Recapture of ammonia and carbon dioxide in a forward osmosis process, MS Thesis, New Mexico Institute of Mining and Technology, Socorro, NM, 2010.

[17] M. Trypuc and U. Kielkowska, Solubility in the NH_4HCO_3 + $NaHCO_3$ + H_2O system, *J. Chem. Engg. Data* 43 (1998) 201-204.

[18] G. W. Gokel, *Dean's Handbook of Chemistry* (2nd ed.), 2004, pp. 4-5.

[19] J. G. Speight, *Lange's Handbook of Chemistry* (16th ed,), 2005, pp. 316-326.

[20] Precision System Inc.TM, OSMETTE A™ Model #5002, Operator's Manual, Automatic High Sensitivity Osmometer, 1994, pp. 1-6.

[21] R. N. Roy, K. Hufford, P. J. Lord, D. R. Mrad and L. N. Roy, The first acidity constants of carbon dioxide in solutions of ammonium chloride from e.m.f. measurements at 278.15 to 318.15 K, *J. Chem. Thermodynamics* 20 (1988) 63-77.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 784-791
Doi: 10.15341/mese(2333-2581)/12.02.2016/004
Academic Star Publishing Company, 2016
www.academicstar.us

A Mathematical Procedure to Estimate Variations between Grain-Size Distributions

Laura Calcagni, Bianca Di Lorenzo, Rossella Di Mento, Ornella Nonnis, and Anna Maria Cicero
Institute for Environmental Protection and Research (ISPRA), Via Vitaliano Brancati, Rome 48-00144, Italy

Abstract: Grain-size is the most fundamental property of sediment particles, its analysis is essential to understand sediment provenance, transport history and depositional conditions. In the ambit of environmental monitoring a key point is often the study of the variations of sediments composition in terms of variation of their grain-size distributions. In this work it is presented a procedure based on the computing of easy mathematical indexes useful to perform in an effective way the comparison of grain-size distributions. The developed procedure consists in two steps of analysis to quantify the dissimilarities between grain-size distributions and to characterize the typology of occurred variations. A validation process is executed to verify the proper work of the procedure, using a large dataset of grain-size distributions.

Two possible applications of the procedure are presented, one to study spatial alterations of sediments composition and another one to analyze temporal changes of sediment in the same sampling station.

The proposed procedure allows to analyze in a quick way large datasets and it is flexible tool to be adapted to the peculiarities of the analyzed data, in order to optimize the achievable results.

Key words: grain-size distributions, Fréchet distance, environmental monitoring

1. Introduction

Grain-size distribution is one of the most important characteristics of sediment; since it characterizes the physical properties of sediment, it determines its provenance, transport history and depositional conditions. In the ambit of environmental monitoring, a key point is often the study of the variations of sediments composition in terms of variation of their grain-size distributions, useful, for example, to model spatial or temporal changes of sediments. In this work it is presented a procedure to perform in an effective way the comparison of grain-size distributions.

2. Fundamentals of Grain-Size Analysis

A grain-size distribution consists in an ordered sequence of values that represent the percentage quantities of granulometric composition of a sediment, expressed by mm (diameter of individual grains) or Φ ($-\log_2$ diameter of individual grains). The comparison of different sediments is dealt with different criteria [1]. In some cases standard statistics of the grain-size distributions such as mean, standard deviation, skewness and a range of cumulative percentile values (e.g., D_{50}) are used as indexes to perform the study of the grain-size variations [2]; these approaches present the limit to not consider all the distribution but only some its aspects, losing the whole characterization of sediments composition. Other authors suggest to analyze the deviation of a grain-size distribution from a prescribed ideal distribution (typically Normal distribution) but in this case it is observed the problem to weight in a different way the different particles diameters [3].

Corresponding author: Laura Calcagni, Ph.D., research areas/interests: numerical modelling; statistical modelling; environmental awareness. E-mail: laura.calcagni@isprambiente.it.

3. Materials and Methods

The aim of this work is to set up a procedure to perform the comparison of grain-size distributions, using parameters easy to compute, without a target ideal distribution in order to not influence the results by a prior fixed model and considering the whole grain-size distribution to have a complete characterization of the sediment.

Let *f, g* be two grain-size distributions, the first index considered to describe their similarity is the maximum difference between all couples of homologous values, that is the points characterized by the same x-coordinate:

$$IM = d_{dM} = max|f_i - g_i| \leq \alpha \quad (1)$$

where i = 1,…,n represents the number of ordinate particles diameters of the grain-size distribution and α is the threshold to discriminate similar or dissimilar distributions; when *IM* index is higher than the threshold α means that grain-size distributions differ of this quantity in one of the analyzed particles diameters. In this way *IM* index is a measure of the variation between two grain-size distributions but it does not provide an indication of the typology of the variation occurred. In the sediments analysis, nevertheless, often it is necessary also to understand the possible cause that determines a grain-size variation, especially if there is a shift of the granulometric peak that is the signal of a deep change in sediments composition. It occurs, for example, in the marine sedimentation strongly influenced by river floods that periodically introduce particles of different diameter. There is the need to deal the study of sediment variations following other approaches, as it is performed also in other ambits of environmental modeling to compare different types of data series by the use of proper metrics [4].

Let now consider two grain-size distributions as two curves, to compute their mutual distance it is possible to apply the Fréchet distance equation that allows to compute the maximal distance between two oriented lines [5]: if *f, g* are the two curves (grain-size distributions) such as $f, g: [0,1]^k \to \mathbb{R}^d, k = 1,2 \ \ k \leq d$, their Fréchet distance is defined as:

$$d_F(f,g) = \inf_{\sigma\ hom} \max_{t\in[0,1]^k} d(f(\sigma(t)), g(\sigma(t))) \quad (2)$$

where σ:$[0,1]^k \to [0,1]^k$ ranges over all orientations preserving homeomorphisms and d is the Euclideian distance. An approximation of the Fréchet distance considered by several authors is the *discrete Fréchet distance* d_{dF}, where the curves are modeled as the ordered sequences of their vertices. Let *P* and *Q* be two polygonal curves given by the ordered sequences of their end points $< p_1 \dots p_m >$ and $< q_1 \dots q_n >$ and let $C =< c_1, \dots, c_k >$ be a coupling of P and Q in an ordered sequences of pairs of vertices, where each c_i has the form $c_i = (p, q)$ with $p \in P$ and $q \in Q$, the discrete Fréchet distance (Eiter et al. (1994)) is defined as:

$$IF = d_{dF}(P,Q) = \min_{Ccoupling} \max_{(p_i,q_i)\in C} \|p_i - q_i\| \quad (3)$$

Also if *IF* is a useful tool to compare two curves measuring their mutual distance, by applying it to quantify the differences between two grain-size distributions, it is pointed out that it does not work properly in some cases, where it does not represent the effective maximum distance between two distributions. In order to understand this, it is necessary to consider carefully its computing process. The Eq. (3) is computed recursively as follows [6]:

$$d_{Fd}(P,Q) = max\left(\begin{array}{c} d_E(P_n, Q_m) \\ min\left(\begin{array}{c} d_{Fd}(< P_1 \dots P_{n-1} >, < Q_1 \dots Q_m >) \forall n \neq 1 \\ d_{Fd}(< P_1 \dots P_n >, < Q_1 \dots Q_{m-1} >) \forall m \neq 1 \\ d_{Fd}(< P_1 \dots P_{n-1} >, < Q_1 \dots Q_{m-1} >) \forall n \neq 1, \forall m \neq 1 \end{array} \right) \end{array} \right) \quad (4)$$

where d_E is an Euclidean distance and d_{dF} is a Fréchet distance. Applying recursively the d_{dF} process with parameters $<P_1 \dots P_{n-1}>$ and $<Q_1 \dots Q_{m-1}>$, the process ends when the two lines are reduced to two single points $<P_1>$ and $<Q_2>$. The recursive computing is performed setting up two matrices whose dimension is $m\ x\ n$, that is the number of vertices of *P* and Q. These matrices are *MD*, the matrix of Euclidean Distance and *MF*, the Fréchet matrix, thus the formula to compute d_{dF}(*P*,Q) can be rewritten as:

$$d_{dF}(P,Q) = \max(d_E(P_i,Q_j), \min(MF_{i-1,j}, MF_{i,j-1}, MF_{i-1,j-1})) \quad (5)$$

The above formula works fixing each time the curve segment to analyze and computing *MD* and *MF* by coupling the segments vertices. Dividing the curves in a sequence of segments, the computing is performed for each couple of segments and the value obtained at the end of the iterative process represents the Fréchet distance. The Fréchet distance thus is the result of a minimization/maximization process of the distances between the vertices of partial segments in which the curves are divided, but this not guarantee that it represents a distance between two homologous points, as it is shown in Fig. 1. This is a limit for the application of Fréchet distance to the study of variations of sediments composition where the comparison has to be limited only to the same particle diameter.

The limit of the application of Fréchet distance to study the variations between grain-size distributions, it is solved through the joint usage of *IM* and *IF* indexes, if they differ there is a shift of granulometric peak. Hence, another index is introduced to study grain-size variations:

$$ID = \frac{1}{\alpha}(IM - IF) = \begin{cases} \in [0,1] \\ > 1 \end{cases} \quad (6)$$

when $ID \in [0,1]$ the variation between two grain-size distributions is due to a percentage change in the granulometric peak or moderate variation in all analyzed fractions; when ID > 1 there is a shift of granulometric peak between the two analyzed distributions. The parameter α is the threshold value used in Eq. (1). The proposed procedure is based on a two steps process, represented in the diagram of Fig. 2. In the first step *IM* index (1) allows to distinguish similar by dissimilar grain-size distributions; in the second step *ID* index (6) provides an indication of the typology of variation.

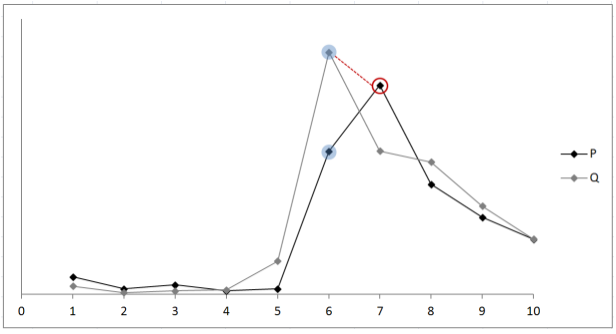


Fig. 1 The Fréchet distance computing respect to the homologous points (same x-coordinate).

4. Validation of the Procedure

The procedure is implemented in a code developed in R language using the package "longitudinal Data", in order to analyze in a quick way also large datasets. The procedure is tested on 180 couples of real grain-size distributions; the threshold α is fixed equal to 10%, since lower variations are considered admissible. In Table 1 are summarized the results obtained at the first step of the procedure, applied to discriminate similar by dissimilar distributions by the use of the *IM* index, almost 50% of the analyzed curves present significant differences. On these curves the second step of procedure is applied, with the results shown in Table 2, in the 92 analyzed curves, 10 present a shift of granulometric peak.

Once completed the procedure for the whole dataset, the obtained results are checked by a visual inspection of the analyzed curves. The possible records of the

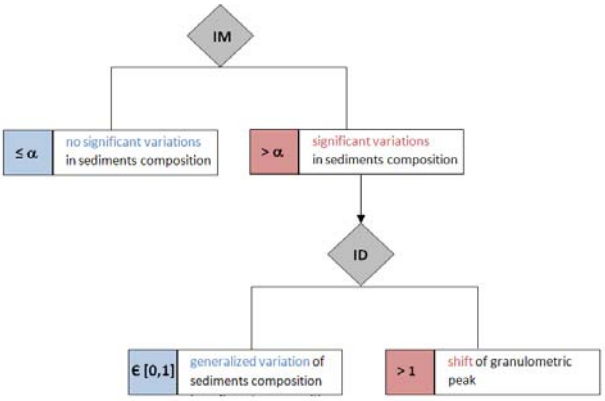


Fig. 2 Conceptual scheme of the procedure.

Table 1 Validation results of the first step of procedure — *IM* index.

couples of grain-size distributions	180
couples with no significant variations ($IM \leq \alpha$)	**88**
couples with significant variations ($IM > \alpha$)	**92**

Table 2 Validation results of the second step of procedure — *ID* index.

curves with significant variations	92
Percentage change of the peak or moderate variation in all analyzed diameters (ID∈[0, 1])	**82**
Shift of granulometric peak (*ID* > 1)	**10**

comparison between couples of grain-size distributions are represented in the Figs. 3-5. In the Fig. 3 it is represented the case of two grain-size distributions that not present significant variations, this is properly signaled by *IM* index that present values lower than the threshold α. The Fig. 4 shows a case where it is obtained a *IM* index greater than the threshold α and a *ID* index equal to 0.23, in the range [0, 1] that represents generalized variations of sediment composition. The graphs of Fig. 5, finally, show the case of the shift of granulometric peak, underlined by a *IM* index greater than the threshold α and the index *ID* > 1, in particular equal to 2.42.

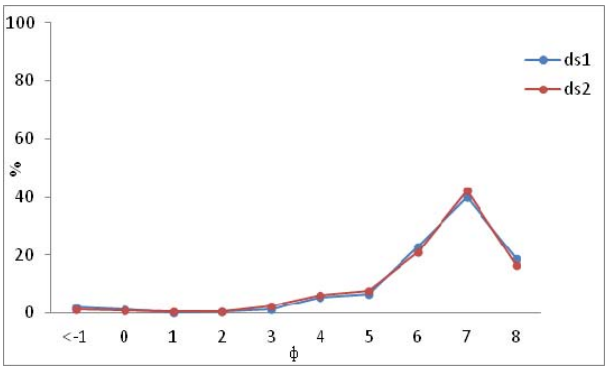


Fig. 3 Case of IM < α, the procedure does not identify significant variations between grain-size distributions.

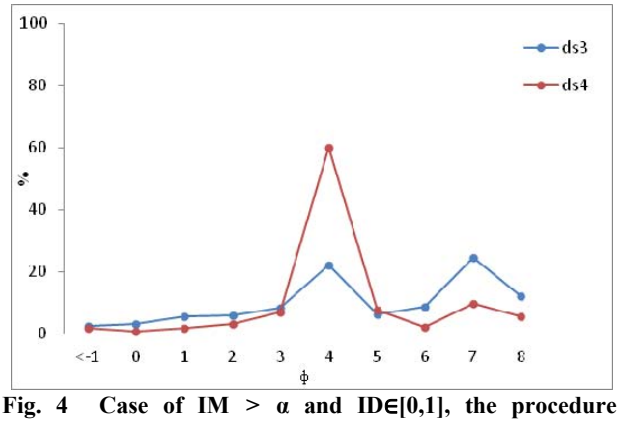


Fig. 4 Case of IM > α and ID∈[0,1], the procedure identifies a generalized variation between the two grain-size distributions.

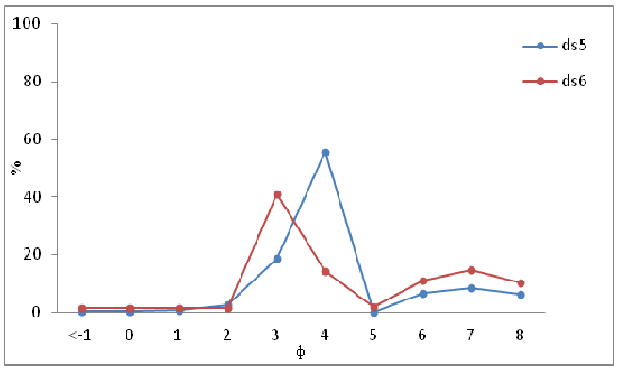


Fig. 5 Case of IM > α and ID > 1, the procedure identifies a shift of granulometric peak.

For all the analyzed grain-size distributions the correct outcome of the procedure is verified, this validation process also allowed to validate the threshold value α, since the chosen value of 10% worked proficiency to discriminate in a proper way similar by dissimilar distributions. This threshold value is independent from the considered dataset.

5. Applications of the Procedure

Two possible applications of the proposed procedure are presented, connected with two different needs of environmental monitoring.

The first application regards the study of spatial variations of sediments characteristics along monitoring transepts, where four stations (P1, P2, P3, P4) are located at different distances, as shown in Fig. 6, an amount of 30 transepts are considered.

The variations of sediments are studied considering the grain-size distributions relative to each monitoring station and coupling them two by two, in this way for each transept 6 couples of distributions are obtained. Fixing a threshold value α equal to 10%, in accord with the results described in the previous paragraph, the *IM* index is computed to each couple of grain-size distributions, and when $IM > \alpha$ also the *ID* index is computed.

The obtained results are summarized in Table 3; for each monitoring transept there are two lines, the first one with the values of *IM* index and the second one with the *ID* index. The values of *IM* index greater than α are underlined by gray color, the red color indicates

the cases where *ID* > 1;; when *IM* index is lower than α the *ID* index is not computed, in accord with the procedure (Fig. 2), and the corresponding cells are empty.

Analyzing the table, since for each transept there are 4 grain-size distributions corresponding to the monitoring stations, each distribution is involved in 3 couples, if all the corresponding *IM* indexes are greater the threshold α means that this distribution differs in significant way by the others, in this way the procedure allows not only to understand that the monitoring transept is characterized by changes in the sediments composition but also to identify the station (or the stations) mainly anomalous. For example, in the transept no. 9 of the Table 3, the station number 1 presents a sediments composition highly different by the others, as it is shown in Fig. 7a.

Furthermore, examining the *ID* index values it also possible to characterize the typology of the variation and if *ID* > 1, as for example in the transept no. 15 of the Table 3, means that a shift of granulometric peak is occurred, in particular in the station number 3 as it is represented in Fig. 7b, it is possible to suppose a different origin of the sedimentation process.

The second application concerns the study of temporal variations of sediments composition. An environmental monitoring plan is performed by periodic surveys of the same area where there are several monitoring points; the data relative to each survey are compared respect to the previous ones in order to underline possible changes.

For example, considering to have for each monitoring point a temporal series of 7 grain-size distributions (c_1, c_2, c_3, c_4, c_5, c_6, c_7), obtained during the surveys of the last seven years, the goal is to compare the grain-size distribution of the current year (c_8) respect to the previous ones. Coupling two by two the eight grain-size distributions it is possible to obtain 28 couples, in seven of them the c_8 distribution is involved, in the 21 remaining it does not.

The *IM* index is computed for all couples of grain-size distributions, in this case it is not compared to a threshold value (1), instead two average values are computed, one relative to the 7 couples that involve the c_8 distribution (*avg_check*) and the other one relative to all other couples (*avg_target*). This is due to the different goal to reach, that in this case is not a

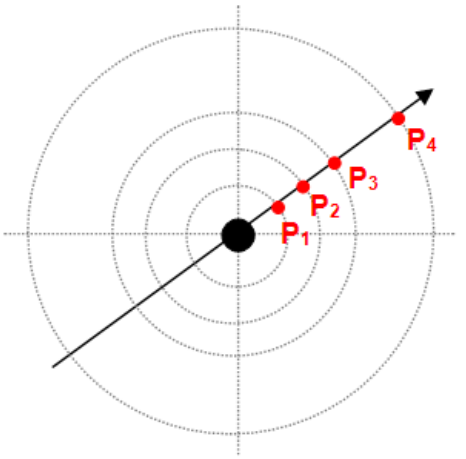
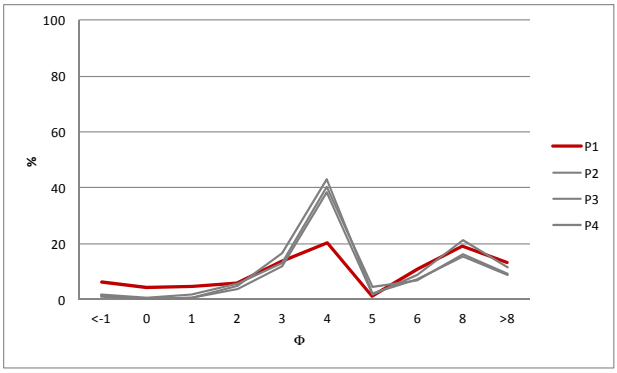
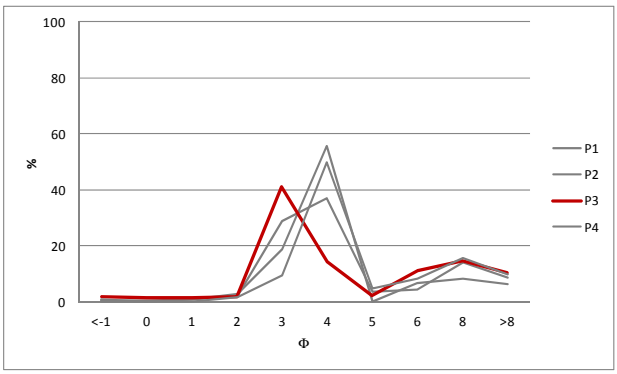


Fig. 6 An example of the considered monitoring transepts.



(a)



(b)

Fig. 7 An example of a two monitoring transepts, one with a station characterized by a different sediments compositions (a) and another one of a transept where a shift of granulometric peak occurred (b).

Table 3 Results of the application of the procedure to the study of spatial variation of sediments composition.

TRANSEPT	INDEX	P1-P2	P1-P3	P1-P4	P2-P3	P2-P4	P3-P4
1	IM	8.72	5.00	5.74	11.13	6.56	8.15
	ID				0.00		
2	IM	18.19	18.10	28.96	6.98	10.77	13.35
	ID	0.00	2.49	0.00		0.00	0.00
3	IM	15.49	5.05	2.08	12.91	15.28	3.88
	ID	0.00			0.00	0.00	
4	IM	4.96	8.32	6.85	9.51	3.42	11.61
	ID						0.00
5	IM	7.72	5.43	6.51	4.95	5.59	2.22
	ID						
6	IM	28.38	28.43	27.47	3.78	10.43	6.77
	ID	0.00	0.00	0.00		0.00	
7	IM	32.12	13.54	7.00	18.58	29.40	10.82
	ID	0.00	0.00		0.00	0.00	0.00
8	IM	8.34	8.76	6.13	7.76	5.52	4.31
	ID						
9	IM	20.10	17.82	22.58	5.12	3.50	5.93
	ID	0.00	0.00	0.00			
10	IM	7.38	31.09	9.70	38.09	14.55	23.54
	ID		13.27		24.87	0.00	14.14
11	IM	18.98	19.56	22.92	2.58	6.37	6.07
	ID	0.00	0.00	0.00			
12	IM	3.21	22.93	8.79	26.14	8.28	20.47
	ID		0.00		0.00		0.00
13	IM	34.23	26.69	27.59	18.11	18.44	5.98
	ID	20.04	16.68	13.07	0.00	0.00	
14	IM	4.47	9.24	23.49	7.75	24.26	16.51
	ID			0.00		0.00	0.00
15	IM	18.41	22.84	19.76	41.25	9.57	35.37
	ID	0.00	10.92	0.00	24.15		25.83
16	IM	12.13	16.80	20.56	5.12	8.43	5.47
	ID	0.00	0.00	0.00			
17	IM	11.52	11.09	12.20	22.61	23.72	5.23
	ID	0.00	0.00	0.00	0.00	0.00	
18	IM	7.91	4.72	13.72	4.84	12.47	12.45
	ID			0.00		0.00	0.00
19	IM	16.67	13.02	13.60	4.55	7.24	3.92
	ID	4.60	0.00	0.00			
20	IM	10.39	6.32	7.61	4.07	4.32	1.45
	ID	0.00					
21	IM	37.84	37.96	27.17	7.60	11.04	10.79
	ID	2.31	2.32	2.26		0.00	0.00
22	IM	19.03	17.25	13.44	12.64	17.37	5.67
	ID	5.41	9.82	4.37	0.00	6.53	
23	IM	8.41	22.63	21.80	17.25	16.42	3.98
	ID		0.00	0.00	0.00	0.00	
24	IM	24.96	22.45	23.79	7.81	11.73	4.93
	ID	0.00	5.30	6.61		3.96	
25	IM	14.52	13.01	12.42	2.17	7.86	6.03
	ID	0.00	0.00	2.35			
26	IM	5.51	12.75	5.94	16.16	10.46	6.88
	ID		0.00		2.35	3.54	
27	IM	3.72	3.50	8.88	4.48	10.80	7.80
	ID					3.59	
28	IM	18.88	9.52	6.94	9.35	14.77	5.42
	ID	12.39				6.42	
29	IM	11.44	23.64	18.27	12.92	7.07	8.84
	ID	0.00	0.00	0.00	0.72		
30	IM	9.83	4.39	2.66	14.23	12.08	2.15
	ID				0.00	0.00	

comparison between two grain-size distributions but is a check of the general trend of a distribution respect to a temporal series of other grain-size distributions. The results are summarized in the Table 4 for each monitoring point.

As it is possible to observe, for each point the *avg_check* are greater than the *avg_target*, this means than the couples that involve the grain-size distribution c_8 present an higher value of *IM* index, thus this distribution differs in a significant way from all the other ones, this means that for this survey a significant change of the sediments is occurred. In Fig. 8 it is represented the situation of one of the monitoring point, as it is possible to observe the grain-size distribution c_8 presents a trend very different from the others.

6. Conclusions

The study of the variations of sediments composition in terms of variation of their grain-size distributions

Table 4 Results of the application of the procedure to a temporal analysis of grain-size data.

Point	avg_target	avg_check
1	21.57	40.98
2	22.02	43.24
3	25.12	37.93
4	22.91	28.38
5	15.78	31.31
6	24.97	35.42
7	25.29	35.57
8	14.34	28.67
9	22.84	29.27

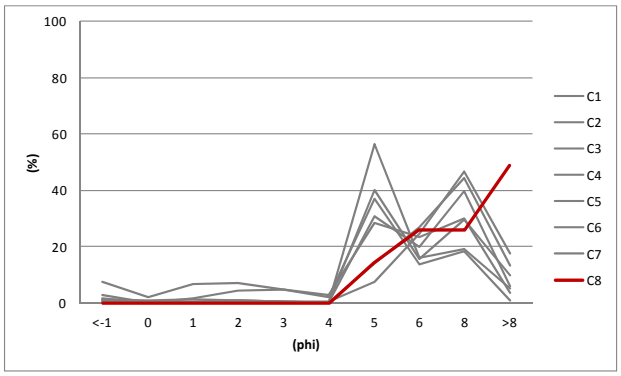


Fig. 8 An example of the temporal variation of grain-size distributions.

plays a key role in the ambit of environmental monitoring, it is thus fundamental to compare in an effective way different grain-size distributions to model spatial or temporal changes of a sediment.

The developed procedure consists in two steps of analysis to quantify the dissimilarities between grain-size distributions and to characterize the typology of occurred variations; the procedure is tested on a large dataset of grain-size distributions.

Two possible applications of the procedure are presented, in two different ambits. It is shown its application to analyze spatial alterations of the sediments composition in environmental monitoring studies, the procedure indexes allow to understand if the investigated transepts are characterized by changes in the sediments composition but also to identify the monitoring stations mainly anomalous. It is also described the usage of the procedure in a temporal analysis of sediments changes, it permits to compare the trend of a grain-size distribution respect to a temporal series of other grain-size distributions relative to the same monitoring point.

The proposed procedure, being based on indexes, is standardized and repeatable; the used indexes are also easy to compute. It allows to analyze in a quick way large datasets and it works properly as shown in the different proposed applications. It is a flexible tool that can be adapted to the peculiarities of the analyzed data to optimize the achievable results.

References

[1] J. S. Blott and K. Pye, Gradistat: A grain size distribution and statistics package for the analysis of unconsolidated sediments, *Earth Surface Processes and Landforms* 26 (2001) 1237-1248.

[2] R. L. Folk and W. C. Ward, Brazos River bar: A study in the significance of grain size parameters, *Journal of Sedimentary Petrology* 27 (1957) 3-26.

[3] J. McManus, *Grain size Determination and Interpretation: Techniques in Sedimentology*, Tucker M. (Ed.), Blackwell: Oxford, 1988, pp. 63-85.

[4] U. Ehret and E. Zehe, Series distance — An intuitive metric to quantify hydrograph similarity in terms of

occurrence, amplitude and timing of hydrological events, *Hydrology and Earth System Sciences* 15 (2011) 877-896.

[5] H. Alt and M. Godau, Computing the Fréchet distance between two polygonal curves, *International Journal of Computational Geometry & Applications* 5 (1995) (1 & 2) 75-91.

[6] A. Mascrete, T. Devogele, I. Le Berre and A. Hénaff, Coastline matching process based on the discrete Fréchet distance, *Progress in Spatial Data Handling*, 2006, pp. 383-400.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 792-799
Doi: 10.15341/mese(2333-2581)/12.02.2016/005
Academic Star Publishing Company, 2016
www.academicstar.us

Determination of Organophosphate Estersin Cigarettes and Cigarette Smoke

Haruki Shimazu

School of Science and Engineering,Kindai University,Osaka, Japan

Abstract: The present study examines the concentration levels of organophosphate esters (OPEs) in cigarettes and cigarette smoke and to know the emission characteristics of OPEs. Seven OPEs were determined in cigarette smokes for five types of Japanese cigarettes. The median total OPE concentrations were 95.5 ng/m^3 before smoking and 282 ng/m^3 after smoking. The median concentrations of tris(2-butoxyethyl) phosphate (TBEP), which was the most abundant OPE, were 68.3 ng/m^3 before smoking and 253 ng/m^3 after smoking. Tris(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPP) were also detected frequently. The relationship between suspended particulate matter (SPM), TBEP, TCEP, and TPP after smoking is significantly proportional. This may indicate that the SPM formation is associated with those OPE formation during smoking. Furthermore, five OPEs were determined in the cigarettes. Median TBEP contents in the cigarettes ranged from N.D. to 9210 ng per cigarette, and the median TBEP emissions from cigarettes while smoking ranged from 3630 to 6730 ng per cigarette. The relationships between TBEP, TCEP and TPP after smoking were significantly positive. The results probably show that parts of TBEP in the cigarettes were transformed to TCEP and TPP, and those OPEs were emitted into the air.

Key words:cigarette, polycyclic aromatic hydrocarbons, sidestream cigarette smoke, suspended particulate matter

1. Introduction

Organophosphate esters (OPEs) are a group of man-made chemicals widely used worldwide as organic plasticizers, flame retardants, hydraulic fluids, antifoaming agents, and for other industrial applications. Global consumption of OPEs has increased from 186,000 to 292,000 tons between 2001 and 2011 [1, 2]. OPEs have been found in various environments, including air [3, 4], indoor air [5, 6], sediments [7, 8], soils [9, 10], and surface water [11, 12].

Some OPEs exhibit carcinogenic or neurotoxic properties. The World Health Organization (WHO) reported that tris(2-chloroethyl) phosphate (TCEP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) were carcinogenic [13]. Tris(2-butoxyethyl) phosphate (TBEP) and tris(2-chloroisopropylethyl) phosphate are suspected carcinogens [13, 14]. TBEP, tributyl phosphate (TBP), TCEP, and triphenyl phosphate (TPP) are all considered neurotoxic [13-16]. Triethyl phosphate (TEP) is thought to be a weak enzyme inhibitor [17]. Therefore, OPEs are drawing attention in many countries. TCEP is on the Candidate List of substances of very high concern issued by the European Union [18]. The use of TCEP, TDCPP, and tris(1-chloro-2-propyl) phosphate (TCPP) as flame retardants in children's products is prohibited or about to be prohibited by the USA and Canada [19, 20].

Many studies have provided evidence that smoking is a major cause of lung cancer [21, 22] and heart disease [23, 24]. Cigarette smoke contains numerous toxic chemicals and carcinogens [25, 26]. This study examined the occurrence of OPEs in Japanese cigarettes and smoke. The primary objective of this work was to determine the concentrations of OPEs in

Corresponding author: Haruki Shimazu, Dr., research areas/interests: environmental engineering. E-mail: hshimazu@civileng.kindai.ac.jp.

cigarette smoke, and identify the emission characteristics of the OPEs.

2. Materials and Methods

2.1 Samples

Five brands of cigarettes were investigated in this study. Tar and nicotine contents per cigarette ranged from 1 to 21 mg and from 0.1 to 1.9 mg, respectively. Table 1 lists the OPE levels in air and cigarette samples before and after smoking.

The numbers of air samples collected for Brands A-D and Brand E were 5 and 4, respectively. The air sampling room was 2.5 m high, 5.3 m in length, and 5.0 m in width (approximately 66 m^3). The air samples were collected at a rate of 400 L/min for 2.0 h (48 m^3) using a high-volume air sampler (HV-500R; Sibata Scientific Technology Ltd., Souka, Japan) before the cigarettes were smoked. A quartz fiber filter (QR-100; Advantec, Tokyo, Japan) was used in the sampler. The filter had a minimum particle collection efficiency of 99.99% for particles 0.3 μm in diameter when air passed through the sampler at a speed of 5 cm/s. After the initial air sampling, two cigarettes were smoked in the sampling room. The sidestream smoke samples were collected at a rate of 400 L/min for 2.75 h (66 m^3). Particulate OPEs collected on the quartz fiber filters were analyzed as described below.

OPEs levels were analyzed in 4 cigarettes per brand. Cigarette filters and leaves were cut into three and six segments, respectively (Fig. 1). A segment of the filters and two segments of the leaves were analyzed as described below.

Table 1 Numbers of air and cigarette samples in this study.

	Air sample		Cigarette sample	
	Before smoking	After smoking	(before smoking)	
			Filter	Leaf
Brand A	5	5	4	8(4×2)
Brand B	5	5	4	8(4×2)
Brand C	5	5	4	8(4×2)
Brand D	5	5	4	8(4×2)
Brand E	4	4	4	8(4×2)
Total	24	24	20	40(20×2)

Note: Two segments of cigarette leaves for cigarette sample were analyzed.

2.2 OPEs

Table 2 lists the targeted seven OPEs in this study; we selected these OPEs because of their known toxic effects.

Seven standard material-grade OPEs were purchased from Tokyo Chemical Industry Co, Ltd, (Japan) and diluted with acetone and hexane, to produce calibration standards.

2.3 Analytical Methods and Instruments

The quartz fiber filters were weighed using an electronic scale before and after smoking. The filterswere cut into 16 segments after smoking. All

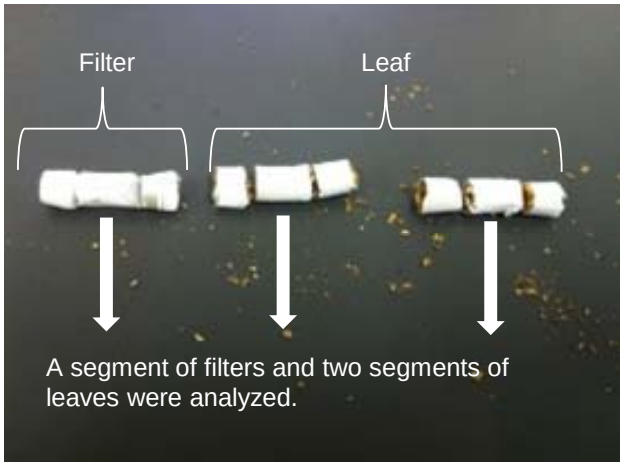


Fig. 1 Analyzed segments of cigarette sample.

Table 2 OPEsmeasured in this study.

OPEs	Abbr	DL
Tris(2-butoxyethyl) phosphate	TBEP	140
Tributyl phosphate	TBP	3.2
Tris(2-chloroethyl) phosphate	TCEP	14
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	170
Tris(2-ethylhexyl) phosphate	TEHP	42
Triethyl phosphate	TEP	6.0
Triphenyl phosphate	TPP	40

Note: The abbreviations are used in this study. The detection limits (DL) were calculated as three times the signal-to-noise ratio at the baseline of the chromatogram. DL units are pg per 2μL-extract.

segments were placed into 260-mL bottles and extracted with 40 mL of dichloromethane for pesticide residue and polychlorinated biphenyl analysis by Wako Pure Chemical Industries, Ltd. (Tokyo, Japan) for 15 min by ultrasonic cleaner. The extract was concentrated to 2 mL using a rotary evaporator, and filtered using a disposable filter device (PURADISCTM 25TF; Whatman, Maidstone, UK). The extract was then concentrated to 0.1 mL under N_2 flow. Next, hexane was added to the extract to produce a final volume of 2 mL.

Cigarette filters and leaves were weighed, placed into cellulose extraction thimbles, and extracted with 40 mL of dichloromethane for 15 min by ultrasonic cleaner. The extract was concentrated to 2 mL using a rotary evaporator, then filtered using a disposable filter and concentrated to 0.1 mL under N_2 flow. Hexane was then added to the extract to produce a final volume of 2 mL.

OPE concentrations in the extracts were determined using a gas chromatography-mass spectrometer (5975B inert XL E/CI MSD; Agilent Technologies, Santa Clara, CA, USA) equipped with an HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness; Agilent Technologies). The GC conditions were as follows: Splitless injection, 2 μL; injection port temperature, 250°C; GC temperature program: 70°C (hold 1.5 min) to 180°C at 20°C/min, and to 280°C at 5°C/min (hold 1 min); the carrier gas was helium. The mass spectrometer was operated in the electron impact mode with an electron energy of 70 eV. After each OPE was identified using three representative fragment ions, it was quantified using the largest one. Quantification was performed using an external calibration method. The detection limits shown in Table 2 were calculated as three times the signal-to-noise ratio at the baseline of the chromatogram. The recoveries and the variation coefficients of the measured OPEs ranged from 70 to 110% and from 5 to 20%, respectively.

Suspended particulate matter (SPM) concentrations were calculated as the difference between the weight of the quartz fiber filters before and after air sampling divided by 48 m^3 (before smoking) or 66 m^3 (after smoking).

3. Results and Discussion

3.1 OPEs in Air Samples

Seven OPEs were detected in the air samples before smoking the cigarettes (Table 3). TBEP, TBP, TCEP, and TEP were detected in all 24 samples. TPP was detected in 15 of the 24 samples. TDCPP and tris(2-ethylhexyl) phosphate (TEHP) were detected in one sample. The median concentration of TBEP, which was the most abundant OPE, was 68.3 ng/m^3, and its concentrations ranged from 28.1 to 246 ng/m^3. The median total OPE concentration was 95.5 ng/m^3, and the total OPE concentrations ranged from 44.2 to 307 ng/m^3.

All seven OPEs were also detected after smoking the cigarettes (Table 4). TBEP, TBP, TCEP, and TPP were detected in all 24 samples. Other OPEs were detected in 19 samples (TEP), three samples (TDCPP), and one sample (TEHP). The median concentration of TBEP, which was the most abundant OPE, was 253 ng/m^3, and its concentrations ranged from 169 to 333 ng/m^3. The median total OPE concentration was 282 ng/m^3, and the total OPE concentrations ranged from 184 to 376 ng/m^3. The concentrations of TBEP, TCEP, and TPP in the air samples were higher after smoking than before. The medians of those concentration differences between before and after smoking were 177 ng/m^3 for TBEP, 3.07 ng/m^3 for TCEP, and 2.18 ng/m^3 for TPP.

The concentrations of TBP, TDCPP, and TEHP before and after smoking were almost identical. However, the concentrations of TEP were higher before smoking than after.

The median concentration of SPM before smoking was 17 μg/m^3, and SPM concentrations ranged from 8 to 30 μg/m^3. After smoking, the median SPM concentration was 117 μg/m^3, and concentrations ranged from 96 to 146 μg/m^3. The relationships between

Table 3 OPEs in air samples before smoking.

	Brand A	Brand B	Brand C	Brand D	Brand E
TBEP	58.0 (5/5) [52.8-108]	55.0 (5/5) [28.1-123]	117 (5/5) [69.5-246]	66.7 (5/5) [48.2-117]	65.7 (4/4) [62.7-115]
TBP	23.7 (5/5) [6.88-27.0]	5.44 (5/5) [3.83-9.60]	13.2 (5/5) [5.84-47.3]	8.28 (5/5) [6.60-11.8]	10.3 (4/4) [9.82-11.3]
TCEP	9.13 (5/5) [7.84-10.1]	6.44 (5/5) [5.13-6.85]	7.35 (5/5) [4.12-7.96]	4.37 (5/5) [2.74-5.91]	13.2 (4/4) [11.6-14.5]
TDCPP	N.D. (0/5) [N.D.]	N.D. (1/5) [N.D.-4.47]	N.D. (0/5) [N.D.]	N.D. (0/5) [N.D.]	N.D. (0/4) [N.D.]
TEHP	N.D. (0/5) [N.D.]	N.D. (0/5) [N.D.]	N.D. (0/5) [N.D.]	N.D. (1/5) [N.D.-0.694]	N.D. (0/4) [N.D.]
TEP	3.77 (5/5) [2.51-5.56]	2.64 (5/5) [1.02-4.29]	5.33 (5/5) [2.58-6.85]	1.05 (5/5) [0.640-2.36]	4.72 (4/4) [3.89-7.41]
TPP	N.D. (0/5) [N.D.]	0.940 (5/5) [0.865-1.13]	0.848 (3/5) [N.D.-1.19]	0.970 (5/5) [0.654-1.26]	1.37 (2/4) [N.D.-3.40]
Σ7OPEs	92.9 (5/5) [73.7-147]	68.0 (5/5) [44.2-149]	141 (5/5) [82.0-307]	87.3 (5/5) [60.6-136]	99.8 (4/4) [88.4-142]

Table 4 OPEs in air samples aftersmoking.

	Brand A	Brand B	Brand C	Brand D	Brand E
TBEP	253 (5/5) [205-265]	259 (5/5) [252-285]	253 (5/5) [221-313]	187 (5/5) [169-240]	294 (4/4) [245-333]
TBP	13.3 (5/5) [7.90-14.3]	10.7 (5/5) [8.03-13.4]	11.5 (5/5) [9.85-38.3]	8.71 (5/5) [6.76-10.9]	14.2 (4/4) [11.8-16.3]
TCEP	14.8 (5/5) [12.2-15.6]	10.3 (5/5) [9.08-11.6]	7.25 (5/5) [6.57-8.89]	4.62 (5/5) [3.01-5.90]	17.3 (4/4) [15.7-18.0]
TDCPP	N.D. (0/5) [N.D.]	N.D. (0/5) [N.D.]	3.22 (3/5) [N.D.-3.33]	N.D. (0/5) [N.D.]	N.D. (0/4) [N.D.]
TEHP	N.D. (0/5) [N.D.]	N.D. (1/5) [N.D.-2.95]	4.45 (5/5) [1.51-6.76]	N.D. (0/5) [N.D.]	N.D. (0/4) [N.D.]
TEP	1.18 (5/5) [0.659-1.90]	N.D. (0/5) [N.D.]	1.33 (5/5) [0.735-1.78]	0.526 (5/5) [0.389-0.579]	1.27 (4/4) [1.02-1.78]
TPP	6.42 (5/5) [5.17-6.96]	3.09 (5/5) [2.96-3.32]	2.32 (5/5) [2.16-3.08]	2.49 (5/5) [1.94-3.06]	8.37 (4/4) [7.40-9.71]
Σ7OPEs	290 (5/5) [231-300]	282 (5/5) [278-313]	306 (5/5) [249-340]	203 (5/5) [184-258]	335 (4/4) [282-376]

Note: The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/m^3. N.D. means not detected. Σ7OPEs means total OPE concentrations.

SPM concentrations and the concentrations of TBEP, TCEP, and TPP, which were detected frequently, were not proportional before smoking. However, the correlation coefficients between SPM and those OPEs after smoking were 0.597 ($p < 0.01$) for TBEP, 0.404 ($p = 0.05$) for TCEP, and 0.438 ($p < 0.05$) for TPP. This may indicate that SPM is associated with the formation of these OPEs during smoking.

3.2 OPEs in Cigarettes

The arithmetic means of the filter weights from the five cigarette brands (n = 4) were 0.24 g for Brand A, 0.25 g for Brand B, 0.25 g for Brand C, 0.24 g for Brand D, and 0.19 g for Brand E. The means for leaf weights were 0.54 g for Brand A, 0.58 g for Brand B, 0.58 g for Brand C, 0.67 g for Brand D, and 0.72 g for Brand E.

Table 5 displays OPE levels in cigarette filters. TCEP and TPP were not detected at all in the 20 samples. Other OPEs were detected in 19 samples (TBP), 12 samples (TEP), seven samples (TDCPP), and five samples (TBEP and TEHP). The median concentration of TBP, which was the most abundant OPE, was 676 ng/g, and TBP concentrations ranged from not detectable (ND) to 14,000 ng/g. The median

total OPE concentration was 3,430 ng/g, and total OPE concentrations ranged from ND to 22,200 ng/g.

Table 6 displays OPE levels in cigarette leaves. TBP was detected in 39 out of 40 samples. TBEP, TEHP, and TPP were detected in multiple samples. The median concentration of TBEP, the most abundant OPE, was 7,100 ng/g, and its concentrations ranged from ND to 24,900 ng/g. The median total OPE concentration was 9,780 ng/g, and concentrations ranged from 250 to 25,700 ng/g. The total concentrations of OPEs in cigarettes were higher in leaves than in filters.

3.3 OPE Emission Characteristics during Smoking

TBEP emission characteristics are described here because TBEP was the most abundant OPE found in our samples. Fig. 2 presents median TBEP contents in cigarettes and median TBEP emissions per cigarette during smoking. TBEP emissions per cigarette were calculated as the difference between concentrations before and after smoking multiplied by 66 m^3 and then divided by two, because two cigarettes were smoked during the experiments. Median TBEP contents ranged from ND (less than about 370) to 927 ng per cigarette for filters and from ND (less than about 700) to 8,410 ng per cigarette for leaves. Median TBEP emissions during smoking ranged from 3,630 to 6,730 ng per cigarette. For Brands A and D, the median of the sum of TBEP contents in cigarette filters and leaves was higher than the median TBEP emissions. For Brand E, the median of the sum of TBEP contents in cigarette filters and leaves was almost identical to the median TBEP emissions. Fig. 3 presents the relationships between TBEP, TCEP, and TPP after smoking for Brands A, D, and E. The correlation coefficients were 0.773 between TBEP and TCEP, and 0.867 between TBEP and TPP. TBEP was detected in cigarettes, but TCEP and TPP were not detected. This may imply that some TBEP in cigarettes was transformed to TCEP and TPP, and these OPEs were emitted into the air during smoking. Although TBEP concentrations in cigarettes were ND for Brand B and very low for Brand C, median TBEP emissions were high. The relationships between TBEP, TCEP, and TPP after smoking were not significant. Therefore, the TBEP production mechanism during smoking for Brands B and C cannot be elucidated from the results of this study.

Further experiments are needed to measure other OPEs in cigarettes and investigate other cigarette brands.

Table 5 OPEs in cigarette filters.

	Brand A	Brand B	Brand C	Brand D	Brand E
TBEP	3620 (3/4) [N.D.-5430]	N.D. (1/4) [N.D.-4320]	1520 (3/4) [N.D.-3190]	1360 (2/4) [N.D.-3910]	N.D. (0/4) [N.D.]
TBP	1160 (4/4) [710-1760]	475 (4/4) [143-642]	206 (4/4) [93.1-818]	1140 (3/4) [N.D.-1390]	3020 (4/4) [331-14000]
TCEP	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]
TDCPP	6410 (4/4) [3740-9240]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D.-493]	1560 (2/4) [N.D.-7590]
TEHP	298 (2/4) [N.D.-1280]	N.D. (0/4) [N.D.]	159 (2/4) [N.D.-1580]	N.D. (0/4) [N.D.]	N.D. (1/4) [N.D.-620]
TEP	57.8 (2/4) [N.D.-159]	118 (4/4) [85.7-146]	113 (3/4) [N.D.-130]	81.9 (3/4) [N.D.-179]	N.D. (0/4) [N.D.]
TPP	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]	N.D. (0/4) [N.D.]
Σ 7OPEs	12000 (4/4) [5610-15800]	698 (4/4) [229-4900]	2230 (4/4) [1950-3410]	2610 (3/4) [N.D.-5900]	4430 (4/4) [635-22200]

Table 6 OPEs in cigarette leaves.

	Brand A	Brand B	Brand C	Brand D	Brand E
TBEP	14700 (8/8) [6800-21400]	N.D. (2/8) [N.D.-1110]	1530 (8/8) [511-23400]	12600 (7/8) [N.D.-15400]	8410 (5/8) [N.D.-24900]
TBP	429 (8/8) [173-955]	310 (8/8) [201-916]	247 (8/8) [175-292]	79.6 (7/8) [N.D.-283]	410 (8/8) [250-10700]
TCEP	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]
TDCPP	N.D. (2/8) [N.D.-1750]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (1/8) [N.D.-1190]
TEHP	715 (7/8) [N.D.-1770]	141 (5/8) [N.D.-263]	146 (5/8) [N.D.-1250]	409 (7/8) [N.D.-906]	392 (5/8) [N.D.-738]
TEP	129 (5/8) [N.D.-309]	68.5 (6/8) [N.D.-97.3]	35.4 (5/8) [N.D.-80.4]	78.7 (5/8) [N.D.-155]	N.D. (0/8) [N.D.]
TPP	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]	N.D. (0/8) [N.D.]
Σ7OPEs	17200 (8/8) [7210-22800]	732 (8/8) [270-1610]	1830 (8/8) [987-24900]	12900 (8/8) [491-16300]	13400 (8/8) [250-25700]

Note: The upper values show median concentration (detection rate) and the lower values show [concentration range]. All units are ng/m^3. N.D. means Not detected. Σ7OPEs means total OPE concentrations.

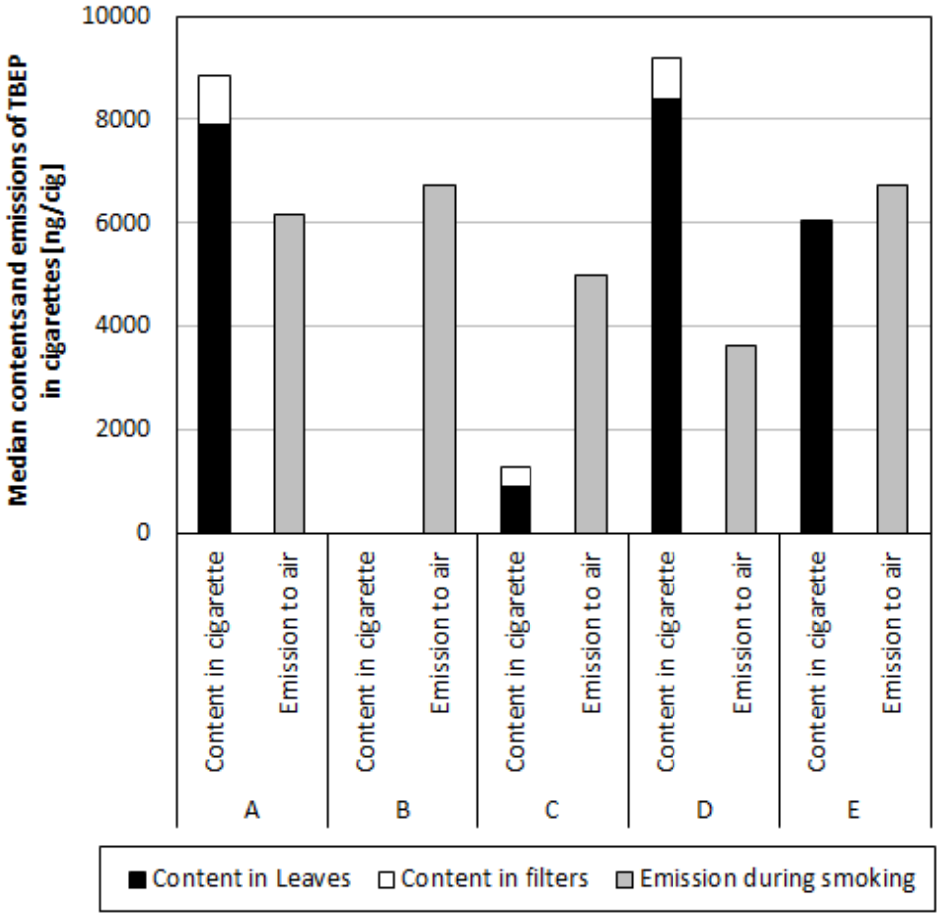


Fig. 2 Comparison of median TBEP contents in cigarettes and median TBEP emissions from cigarettes during smoking for Brands A–E. Solid bars and open bars show contents for leaves and filters

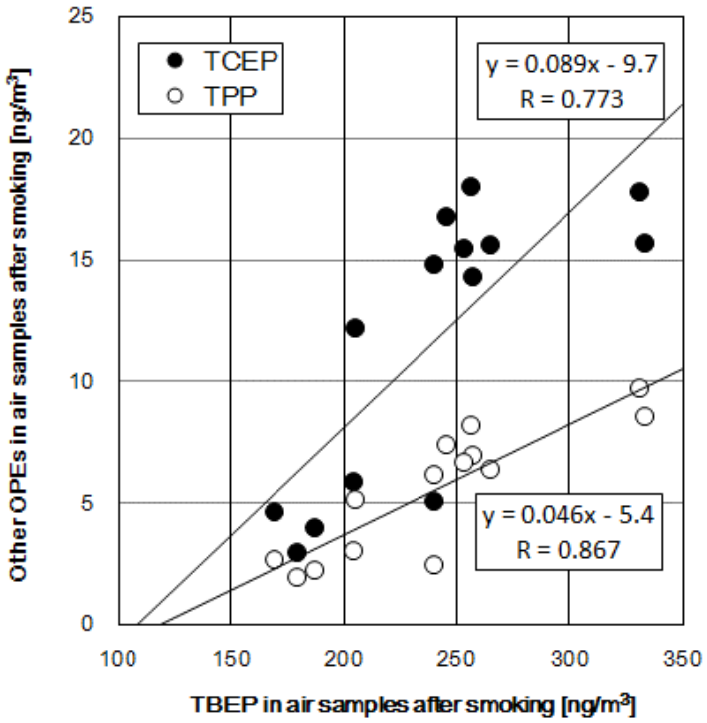


Fig. 3 Relationship between TBEP, TCEP, and TEP in air samples after smoking.

4. Conclusions

Seven OPEs in five cigarette brands and their formation and emissions during smoking were investigated. OPEs were measured in air samples before and after smoking. TBEP was the most abundant OPE detected. Significant proportional relationships were observed between SPM concentrations and the concentrations of TBEP, TCEP, and TPP after smoking. This may indicate an association between OPE formation during smoking and SPM.

Five of the OPEs were also detected in the cigarettes. The concentrations and contents of total OPEs were higher in cigarette leaves than in cigarette filters.

In several brands of cigarettes, the relationships between TBEP, TCEP, and TPP after smoking were significantly positive. TBEP was detected in cigarettes, but TCEP and TPP were not detected; this may imply that some TBEP is transformed to TCEP and TPP during smoking.

References

[1] A. Marklund, B. Andersson and P. Haglund, Organophosphorus flame retardants and plasticizers in Swedish sewage treatment plants, *Environ. Sci. Technol.* 39 (2005) 7423-7429.

[2] Townsend Solutions, *Plastic Additives 8 Global Market Study*, 2012.

[3] A. Salamova, M. H. Hermanson and R. A. Hites, Organophosphate and halogenated flame retardants in atmospheric particles from a European arctic sites, *Environ. Sci. Technol*. 48 (2014) 6133-6140.

[4] S. Lai, Z. Xie, T. Song, J. Tang, Y. Zhang, W. Mi, J. Peng, Y. Zhao, S. Zou and R. Ebinghaus, Occurrence and dry deposition of organophosphate esters in atmospheric particles over the northern South China Sea, *Chemosphere* 127 (2015) 195-200.

[5] M. A. Abdallah and A. Covaci, Organophosphate flame retardants in indoor dust from Egypt: Implications for human exposure, *Environ. Sci. Technol.* 48 (2014) 4782-4789.

[6] F. Yang, J. Ding, W. Huang, W. Xie and W. Lei, Particle size-specific distributions and preliminary exposure assessments of organophosphate flame retardants in office air particulate matter, *Environ. Sci. Technol.* 48 (2014) 63-70.

[7] Y. Kawagoshi, I. Fukunaga and H. Itoh, Distribution of organophosphoric acid triesters between water and sediment at a sea-based solid waste disposal site, *J. Mater. Cycles. Waste Manag.* 1 (1999) 53-61.

[8] H. W. Chung and W. H. Ding, Determination of organophosphate flame retardants in sediments by microwave-assisted extraction and gas chromatography–mass spectrometry with electron impact and chemical ionization, *Anal. Bioanal. Chem.* 395 (2009) 2325-2334.

[9] E. Fries and I. Mihajlovic, Pollution of soils with organophosphorus flame retardants and plasticizers, *J. Environ. Monit.* 13 (2011) 2692-2694.

[10] H. Shimazu, T. Shibata, T. Horie, Bioaccumulation characteristics of organophosphoric acid triesters and polycyclic aromatic hydrocarbons in *Phragmites*, *J. Water Environ. Technol.* 11 (2013) 287-297.

[11] J. A. Andresen, A. Grundmann and K. Bester, Organophosphorus flame retardants and plasticisersin surface waters, *Sci. Total Environ.* 332 (2004) 155-166.

[12] E. Martínez-Carballo, C. González-Barreiro, A. Sitka, S. Scharf and O. Gans, Determination of selected organophosphate esters in the aquatic environment of Austria, *Sci. Total Environ.* 388 (2007) 290-299.

[13] WHO, Flame Retardants: Tris(chloropropyl) phosphate and tris(2-chloroethyl) phosphate, *Environmental Health Criteria 209*, 1998.

[14] WHO, Flame Retardants: Tris(2-butoxyethyl) phosphate, tris(2-ethylhexyl) Phosphate and tetrakis (hydroxymethyl) phosphonium salts, *Environmental Health Criteria 218*, 2000.

[15] WHO, Tributylphosphate, *Environmental Health Criteria 112*, 1991.

[16] WHO, Triphenylphosphate, *Environmental Health Criteria 111*, 1991.

[17] R. E. Gosselin, R. P. Smith, and H. C. Hodge, *Clinical Toxicology of Commercial Products* (5th ed.), Baltimore, 1984, p. II-302.

[18] European Chemicals Agency, *Inclusion of Substances of Very Concern in the Candidate List*, 2009.

[19] TÜV Rheinland Group, *US Tightens Requirements on Flame Retardants for Children Products*, 2013.

[20] Health Canada, *Regulations Amending Schedule 2 to the Canada Consumer Product Safety Act (TCEP)*, 2014.

[21] C. H. Lee, Y. C. Ko, L. S. Cheng, Y. C. Lin, H. J. Lin, M. S. Huang, J. J. Huang, E. L. Kao, H. Z. Wang, The heterogeneity in risk factors of lung cancer and the difference of histologic distribution between genders in Taiwan, *Cancer Causes Control.* 12 (2001) 289-300.

[22] IARC, Tobacco smoke and involuntary smoking, *IARC Monographs on the Evaluation of the Carcinogenic Risks to Humans*, 2004, p. 83.

[23] A. C. Villablanca, J. M. McDonald and J. C. Rutledge, Smoking and cardiovascular disease, *Clin. Chest. Med.* 21 (2000) 159-172.

[24] B. Messner and D. Bernhard, Smoking and cardiovascular disease — Mechanisms of endothelial dysfunction and early atherogenesis, *Arterioscler. Thromb. Vasc. Biol.* 34 (2014) 509-515.

[25] IARC, Overall evaluations of carcinogenicity: an updating of IARC monographys, Vols. 1-42, Suppl. 7. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, 1987.

[26] IARC, Some non-heterocyclic polycyclic aromatic hydrocarbons and some related exposures. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, 2010, p. 92.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 800-808
Doi: 10.15341/mese(2333-2581)/12.02.2016/006
Academic Star Publishing Company, 2016
www.academicstar.us

Photocomic Narratives as A Means to Communicate Scientific Information about Use, Treatment and Conservation of Water

Cecilia Lartigue, Aquiles Negrete, Eduardo Velasco, and Fernando González Villarreal
Universidad Nacional Autonoma de Mexico (UNAM), Mexico

Abstract: In this research we propose that photocomics represent an opportunity to communicate scientific information to students in a reliable and economic way. We used these narratives to communicate information about efficient water management activities and also to publicize PUMAGUA, the Program of the Autonomous National University of Mexico (UNAM) in charge of water management at the University. Using the Retell, Identify, Remember and Contextualize information (RIRC) method (a method that uses memory tasks to assess learning) we tested the efficiency of this kind of illustrated narratives to communicate scientific information. We found statistical evidence that students acquired information regarding water use using this media and we also found statistical differences in performance between the participants of different schools at the main campus of UNAM.

Key words: narratives, photocomics, science communication, water conservation, water management

1. Introduction

While human population worldwide tripled in the last century, the use of water resources grew six-fold. Within the next fifty years, the world population will increase by another 40 to 50%. This increase, together with industrialization and urbanization, will result in a growing demand for water [1]. Strategies for efficient water management are urgently needed throughout the world, particularly in regions with high water stress. By 2025, 1.8 billion people will be living in countries or regions with severe water scarcity, and two-thirds of the world's population could be living under water stressed conditions [2]

In the case of Mexico, although it is ranked number 53 in the world in terms of water stress [3] most of its territory suffers from medium-high to very high stress.

In order to contribute to water conservation in Mexico, in 2008, the National University of Mexico (UNAM) launched the Program for Water Management, Use and Reuse (PUMAGUA) with three main objectives: (1) to reduce water consumption by 50%; (2) to improve the quality of drinking and treated wastewater according to the most strict water quality norms; (3) to promote participation of the entire population of the university in the efficient use of water. The Program started at the main campus in Mexico City and has progressively been implemented at other campuses of the UNAM.

To achieve the third objective of PUMAGUA, a communication/participation program was implemented, which includes innovative and participative activities to promote successful practices of water conservation, such as workshops, artistic contests, festivals, concerts, and print products, among them photocomic narratives.

Narratives are particularly important in Mexico, as they represent an informative vehicle for anyone who has left the classroom years ago and needs to be updated, as well as for teaching students in the classroom [4-8]. Narratives provide a precise tool with

Corresponding author: Aquiles Negrete, Ph.D., research areas/interests: science communication, science education, narratives, cultural media. E-mail: aqny@unam.mx.

which to represent and transmit knowledge; they are an effective emotional detonator, a long term mnemonic structure, and an important reinforcement for learning [9] Stories enhance the process of communication and are fundamental both at the level of the community and of the individual[10]

The presentation of scientific information by means of short stories, novels, drama and comic strips should be considered as an important resource for the dissemination of knowledge, among the range of instruments at the disposal of science communicators and writers [11]. Comics are a popular art form and provide a potential medium for science education and communication [12]. Years of research in pedagogy have shown that text and illustrations work well together to improve instruction [13]. The advantage of using comic strips to communicate information is that they induce the use of several parts of the brain, allowing the reader to catch textual sequential information besides the visual holistic information [14]

Early studies have shown the effectiveness of comic strips to convey knowledge and practices related to particular scientific concepts [15-16]. They have been particularly helpful in health and science learning sectors. In Egypt, for instance, the World Health Organization used them to disseminate knowledge about lymphatic filiasis (a disease that can lead to elephantiasis) and to reduce stigma towards people who had developed elephantiasis [17]. In China, they were successfully used, together with a cartoon video, to explain the transmission of schistosomiasis, as well as to discourage children from playing in known infected waters [18]. In the United, comics conveyed information regarding health risks from contact with pesticides, as well as proper use and storage of these products [19].

With regards to science learning, Hosler and Boomer [13] proved the effectiveness of a comic book to disseminate knowledge and positive attitudes towards Biology. In this study a questionnaire was applied before and after exposure to the comic book in the classroom. These authors found that an increase in knowledge was particularly high in students who had shown the lowest performance in the class before exposure to the comic book.

In Mexico, comic strips (and photocomics) are a cultural narrative medium that is deeply established in national culture, as it is the principal access to reading for millions of inhabitants. This is the case of more than one third of Mexicans between 12 and 22 years of age [20]. Photocomics are a particular kind of comic strip where the images are photos rather than drawings; they are also very popular among the population.

Although Mexico is a country in which the reading rate is low, if we take into account the total population we find that the absolute number of readers is considerable. By and large, what the Mexican public reads are superficial and disposable texts [21]. Evidence of this can be found in the high press runs of magazines covering entertainment gossip, fashion, and comic strips with stereotyped storylines (sex, crime or pseudo westerns). Nowadays, comic strips are one of the preferred media and the principal access to reading for millions of Mexicans. In the last decade they represented around 33.5% of total publications in this country [20].

The fact that comic strips (photocomics) already have a great appeal among a broad sector of the population makes them a very attractive medium to reach numerous segments of society. If we are capable of designing a tool, suitable for transmitting scientific information about water use, treatment and conservation, that achieves a positive impact and stimulates individuals to avoid waste, we will contribute significantly to social well-being.

In order to measure the effects of the photocomic in the retention of scientific information, the RIRC method [11] was employed to evaluate the comprehension and retention of scientific knowledge. The RIRC method explores the effectiveness of a narrative (and other formats) for communicating scientific information using four independent memory

tasks to assess learning. This method assesses an individual's ability to retell, identify, remember and contextualize scientific information presented to them in narrative form. The input consists of a qualitative complex stimulus (a story narrative or another text format) and the outcome is measured using questionnaires.

2. Material and Methods

The basis for the development toward energy saving under economic points of view are the classification and the comparison of the energy demand of the agricultural operation and the single aggregates with the certain specific operating reference values of the plant.To establish an exact and differentiated database to the analysis of the single production processes energy consumption values dependent on procedure of single consumers (devices and machines which are fused in the electric distribution separately, e.g., vacuum pump and cooling aggregate in dairy farms)and consumer groups(summary of several single consumption components to a consumption group, e.g., airing control, engines for regulating flaps, fans in the consumption range ventilation or all luminous units of the stable in the consumption area lighting) are evaluated and measured.

We adapted a script (that had originally been written for a short film by Biology undergraduate students of the UNAM) to a photocomic (Appendix I). The plot is about a girl that bumps into her friend and they decide to go together to print her thesis n on the university campus. First they go to the toilet, where her memory stick (USB) with the dissertation falls into the toilet. The search for the memory stick serves as an excuse to show the water management system at the campus, as well as PUMAGUA specific actions to improve water use.

Copies of the photocomic were presented to seven classes of undergraduate students, each belonging to a different school at the UNAM. Students read the narrative and subsequently answered a questionnaire with ten questions regarding technical information about the water management system and PUMAGUA's actions (Appendix II). Using the RIRC method, questions were designed to measure memory tasks regarding the information presented in the photocomic: four questions concerning identification, three regarding recall, and one to test the ability to contextualize the information. In order to identify the issues that were known beforehand and therefore to avoid overestimating the effect of the narrative on individuals' knowledge of the subject, the five students randomly selected in each group (control group) were asked to answer the questionnaire without first reading the photocomic.

Responses to questions 1 to 9 (identifying and remembering) were marked in a binary way (correct or incorrect), while answers to question 10 (contextualize), were analyzed using two methods. First, answers were coded using the following categories: (a) answers referred to the information contained in the narrative and reflected that the information was well understood, (b) answers were ambiguous (not clear if the information was correctly understood), (c) answers were imprecise or unrelated to the photocomic, (d) answers were wrong, or (e) the question was not answered.

The second method involved the following: the words included in the answer to question 10 were analyzed to determine if they were those used originally in the narrative. Also synonyms were extracted, as well as other words that did not appear in the photocomic, but belong to water management jargon.

The following table (Table 1) includes the list of themes that we wanted to convey to the students (active principles) through the photocomic, as well as the specific question of the questionnaire that inquires about each theme.

3. Results and Discussion

The students that voluntarily collaborated in this

study belonged to the schools of Accounting, Chemistry, Earth Sciences, Engineering, Political Sciences, Philosophy, and Psychology of the UNAM. A total of 312 undergraduate students participated, 172 females and 140 males ranging from 18 to 23 years of age. From this sample 277 read the photocomic and answered the questionnaire and 35 only answered the questionnaire (control group) (Table 2).

Table 1 Themes included in the photocomic "The Mystery of the USB" and number of question of the questionnaire addressing each theme.

Theme	Description	Question addressing each theme
Water management system	Extraction, distribution, consumption, treatment, and reuse of water	1
Safe drinking water	Disinfection system and consumption in water fountains	3,10
Safely treated wastewater	Treatment plant with innovative process and safe use of treated wastewater to irrigate gardens	5,10
Water conservation actions	Toilet retrofit, reporting leaks, hygiene actions	7,8
PUMAGUA actions	Toilet retrofit, water disinfection system	6

Table 2 Number of students from each school that read the photocomic.

School	Number of participants
Accounting	50
Chemistry	20
Earth Sciences	51
Engineering	34
Political Sciences	17
Philosophy	55
Psychology	50
Total	277

Two different statistical analyses were conducted: T-tests were calculated to assess the effectiveness of the photocomic to convey information about water management and ANOVAs were calculated to assess the difference in knowledge acquisition between participants from different schools. When statistical differences were found post hoc, comparisons using Sceffé's method for a single-step multiple comparison were performed in order to determine which schools were responsible of the differences.

Table 3 and Fig. 1 present a comparison of answers to each question between participants that read the photocomic and those that only answered the questionnaire. There were significant differences in both the mean of correct answers to each question and the overall score, with participants who read the photocomic scoring higher score than those who did not.

Table 3 Comparison of correct answers between participants who read the photocomic and those who did not.

	Reading the photocomic (N = 277)	Not reading the photocomic (N = 35)	t	p
Means (Standard deviations)				
Question 1	0.80 (0.397)	0.03 (0.164)	22.112	.000***
Question 2	0.69 (0.462)	0.16 (0.136)	7.939	.000***
Question 3	0.91 (0.286)	0.57 (0.502)	4.073	.000***
Question 4	0.44 (0.497)	0.08 (0.227)	6.634	.000***
Question 5	0.92 (0.227)	0.51 (0.507)	4.756	.000***
Question 6	0.95 (0.221)	0.57 (0.502)	4.564	.000***
Question 7	0.95 (0.214)	0.35 (0.484)	7.462	.000***
Question 8	0.22 (0.418)	0.00 (0.000)	9.485	.001***
Question 9	0.88 (0.331)	0.54 (0.505)	3.928	.000***
Question 10	0.66 (0.473)	0.22 (0.417)	6.072	.000***
Mean of overall score	0.74 (0.167)	0.30 (0.123)	19.617	.000***

*p ≤ .05, **p ≤ .01, ***p ≤ .001

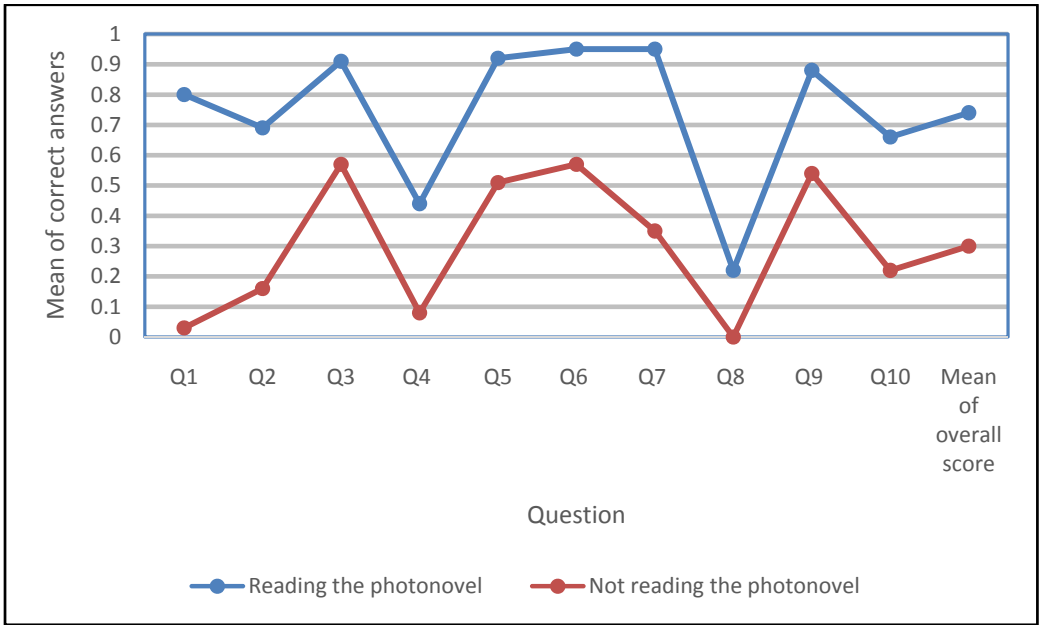


Fig. 1 Differences in correct answers and overall score between participants that read the photocomic and those who did not.

The regular cleaning, servicing and inspection of the ventilation system should take place at least semi-annual. To this the temperature sensors must be calibrated if necessary and all regulating systems should be optimally adjusted. By regular cleaning all supply and exhaust air ducts, ventilating fans and airing flaps the unnecessary pressure losses to be compensated by the ventilation system which lead to an increase of the power consumption can be avoided. The examination and if necessary the adaptation of the climate rated values to seasonal aerial change variations and the growth curve of the animals also belongs to a regular servicing. Thus an efficient operation of the ventilation system can be ensured.

With regard to the difference in knowledge acquisition between participants from several schools of the UNAM (Fig. 2), ANOVAs were calculated for each of the ten questions and for the overall score. By conducting Scheffe's post hoc method, significant differences were found in four questions and the overall score, as follows:

(1) Question 2. [F: (6/305) = 7.26, p=.000***], between the groups of Philosophy (= 0.85), Earth Sciences (= 0.82), Accounting (= 0.48), and Political Sciences (= 0.46).

(2) Question 4. [F: (6/305) = 4.33, p = .000***]: between the groups of Philosophy (= 0.60), Chemistry (= 0.70), and Psychology (= 0.27).

(3) Question 8: [F: (6/305) = 277.455, p = .000***]: between the groups of Philosophy (= 0.50), Accounting (= 0.40), Engineering (= 0.38), Earth Sciences (= 0.37), Political Sciences (= 0.29), and Chemistry (= 0.30).

(4) Question 10: [F: (6/305) = 249.619, p = .050*]: between the groups of Philosophy (= 0.84), and Accounting (= 0.56). Overall score [F: (6/305) = 7.26, p = .000***]: between the groups of Philosophy (= 0.84), Earth Sciences (= 0.70), Accounting (= 0.71), and Political Sciences (= 0.67).

Question 10 was answered by over 90% of respondents. To the question "Which aspects should you monitor in order to decrease the incidence of these diseases?" almost half of the answers were classified as option (a), i.e., "clear", which revealed understanding of the information contained in the narrative (Fig. 3). Examples of these were: "The disinfection system to see if it was working properly", "I would check if there is no risk from watering gardens with treated waste

water and that the treatment plant is working properly", or "That the irrigation water is not used for drinking". However, there were many cases where there was a high number of imprecise answers or the technical information was only slightly related to the comic. For instance some responded with short phrases such as "Water quality", "Purification", or "That filters are O.K.".

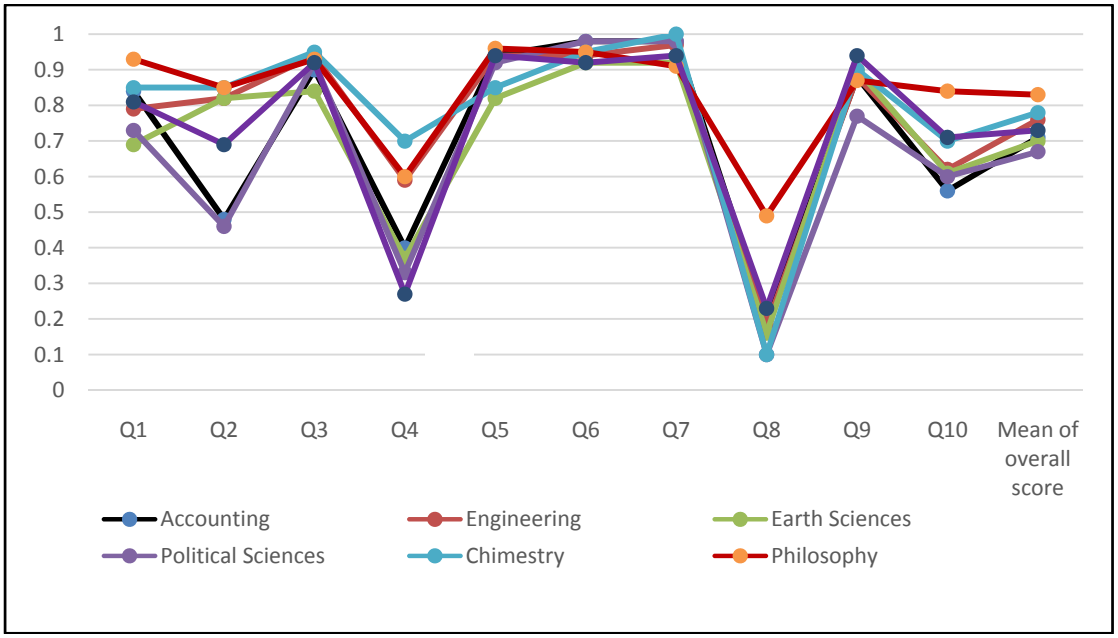


Fig. 2 Means of correct answers according to participants' schools.

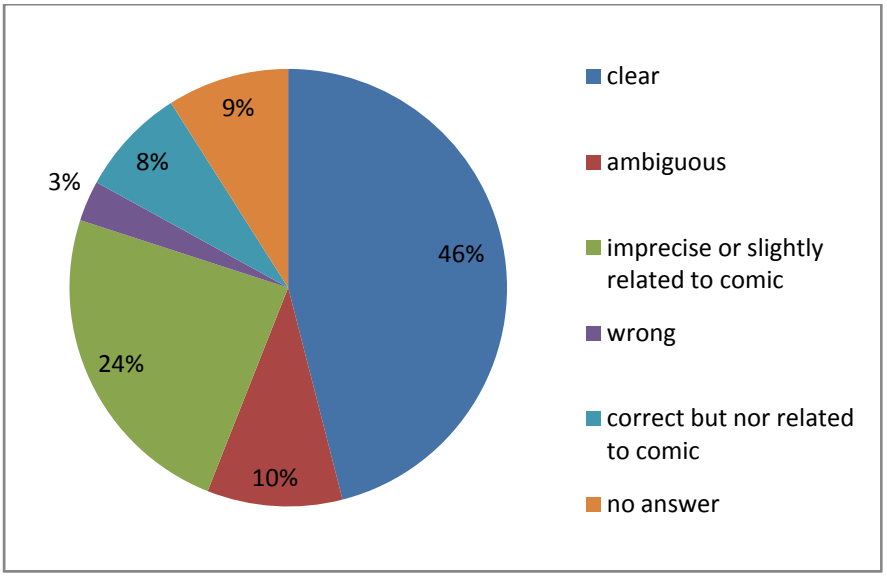


Fig. 3 Percentage of types of answers to contextualize question 10.

In 10% of responses, the answers were evaluated as "ambiguous", because apparently there is some confusion between the wastewater treatment plant used to produce water for irrigation and the disinfection system that provides drinking water. For instance in the answer "the process of the disinfection system, the filters, that the system is working properly" it seems as if the filters belong to the disinfection system while the photocomic mentions them as part of the wastewater treatment plant.

Eight percent of the answers were correct but the information did not come from the photocomic ("That the water tanks are clean", "Those students have good hygiene practices", "To fire the people in charge of the water system because they clearly do not care"). Less than 5% were wrong, like the following: "I would monitor the water treatment plant of the ultrafiltration membranes coming from the three wells". The respondent confused drinking water coming from the wells with wastewater treated with ultrafiltration membranes in the treatment plant. Other respondents confused the information that was used only as part of the literary plot, i.e., dropping the USB containing the thesis into the toilet.

Finally, it is worth mentioning that some answers were considered incorrect not because the information in the narrative was misunderstood but because it was not included in the photocomic. For instance: "I would make sure that water is not used to drink but instead that it is used in laboratories, toilets and irrigation". This is incorrect on two levels: first, because water that comes in contact with human skin, such as water used in laboratories, toilets and for watering purposes, must be free of pathogens. In addition, as mentioned beforehand, this information was not provided by the narrative.

When comparing answers to question 10 among participants of different schools, Philosophy had the highest percentage of clear answers, followed by Earth Sciences and Engineering, while Political Sciences performed the worst, and also had the highest number of ambiguous answers (Fig. 4).

Finally, the analysis of words most frequently used to answer question 10 showed that the ones best retained from the photocomic where water fountains, treatment plants, filters, treatment and disinfection system (Fig.5). As presented in Table 1, question 10 addressed two themes: safe drinking water and safe treated wastewater. Therefore, the words most frequently used corresponded to both subjects. In the case of safe drinking water, both the system that makes it safe (disinfection system) and the consumption point (water fountains) were pointed out, while in the case of safe treated wastewater, the system was repeatedly mentioned (treatment plant, filters, treatment), but the point of use (gardens) was scarcely cited. This is probably due to the fact that water fountains appeared at the beginning of the narrative, while gardens appeared in the last part of it. This matches with Negrete's observation that the closer the scientific information comes to the important moments in the narration (e.g., revelations, peripetia, anagnorisis, outcome, central functions, etc.), and the higher in hierarchy with respect to the plot, the more likely it is to succeed in being communicated and recalled [9].

Participants that read the narrative had a higher performance in all the tasks of the questionnaire than those that did not read it, regardless of the kind of questions (identify, remember, recall or contextualize). These results suggest that the photocomic generated in this research was effective in communicating technical information about water use.

4. Future Work and Research

Given the constraints of photocomics in terms of text extension and use of technical jargon, an important challenge for future work is to create one narrative that takes into account concepts found in this study that are either ignored or misunderstood by the public (e.g. differences between waste water and drinking water treatment systems, quality requirements for different uses of water). Given that water management in Mexico City is a subject of public concern, people have preconceived ideas about it, some of them incorrect. This can prove challenging because it is often more difficult to replace people's wrong ideas with right concepts than to convey information to a non-misinformed population.

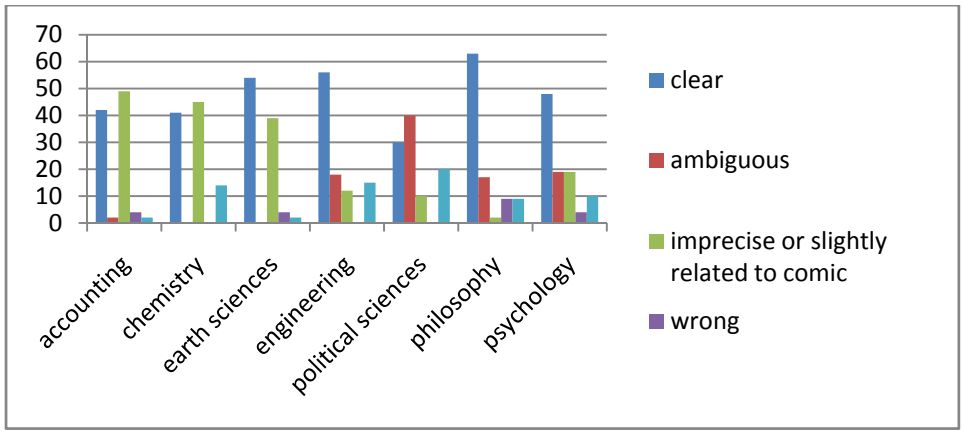


Fig. 4 Comparison between schools of types of answers to question 10.

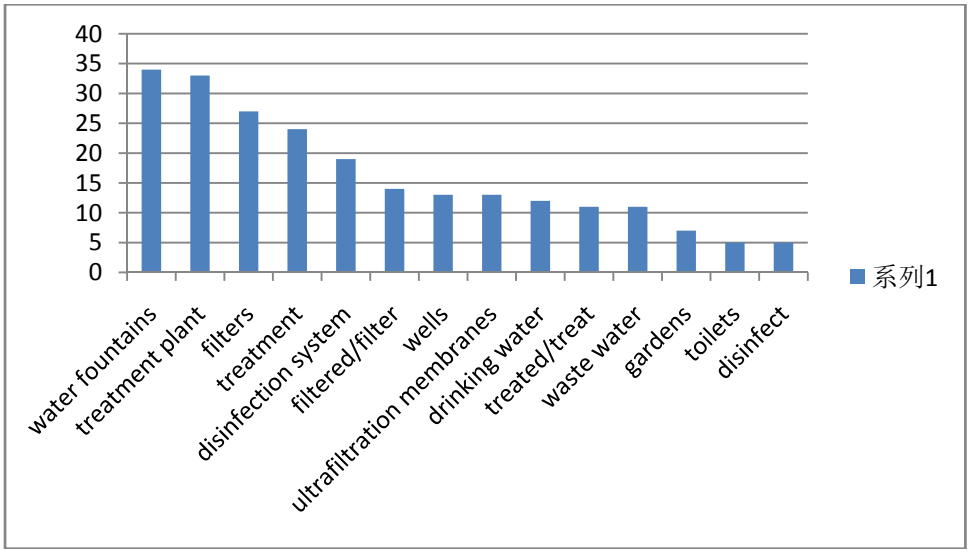


Fig. 5 Frequency of technical words most used in answers to question 10.

In a future study it would be desirable to evaluate if this knowledge persists over time and also to compare effectiveness and memorability between this photocomic and a non-narrative means, such as textbooks, technical reports, etc. According to Negrete (2009) narratives are equally efficient as non-narrative means in conveying scientific information, but are more memorable. In said study, the narratives used as stimulus were short stories (op cit). It is likely that photocomics are even more memorable because information provided by text is reinforced by images. As previous studies have asserted, words associated with imagery are learned more easily than those without [22].

When comparing knowledge acquisition between participants of different schools of the UNAM, a difference was detected only between Political Sciences and Philosophy. This may be explained by the fact that students of the latter are more used to reading narratives than those of political sciences.

It would be desirable to create more photocomics (1) to further explore the differences in learning processes between the various schools at the main university campus and (2) to reach other publics at the UNAM that need to be conscious of water conservation practices, such as gardeners, janitors and staff in laboratories. For the latter, a study of these audiences' narrative preferences should be carried out; it is foreseeable that the components of the narrative (the characters, plot, structure and language depicted in

such narratives) should be modified to successfully reach such groups.

5. Conclusion

The findings of this research as a whole suggest that photocomics are an effective means to communicate scientific information to the public with socially worthwhile messages. In this research we propose that popular photocomics can, for certain student audiences, be used as a tool to communicate scientific information in an understandable, memorable and enjoyable way. In the case of Mexico, they represent a unique opportunity to communicate scientific information about natural resources conservation to a large sector of the university population, often very difficult to reach through other means.

Acknowledgements

The photocomic was inspired by a script written by Sol Guerrero and Claudia Becerril. Berenice Hernández, Guillermo Montero, and Analleli Camacho participated in the creation of the photocomic. The narrative and the questionnaire were applied to students by UNAM lecturers Rocío Carranza, Malinali Domínguez, Beatriz Ortega, Adriana Palma, and Mauricio Ricardez.

References

[1] World Water Council, Water Crisis, 2014, available online at: http://www.worldwatercouncil.org/library/archives/water-crisis/.

[2] United Nations Water (2014), Statistics, available online at: http://www.unwater.org/statistics/en/?page=4&ipp=10&tx_dynalist_pi1%5Bpar%5D=YToxOntzOjE6IkwiO3M6MDoiIjt9.

[3] Comisión Nacional del Agua (CONAGUA 2014), Atlas Digital del Agua. Available at: Atlas Digital del Agua Sistema Nacional de Información del Agua, available online at: http://www.conagua.gob.mx/atlas/aguaenelmundo51.html.

[4] N. Gough, *Laboratories in Fiction: Science Education and Popular Media*, Geelong: Deakin University, 1993b.

[5] P. M. Appelbaum, *Popular Culture, Educational Discourse, and Mathematics*, NY: State University of New York Press, 1995.

[6] M. Weinstein, Robot world, in: *Education, Popular Culture, and Science*, NY: State University of New York Press, 1998.

[7] J. Weaver, Synthetically growing a post-human curriculum: Noel Gough's curriculum as a popular cultural text, *Journal of Curriculum Theorising* 15 (1999) (4).

[8] A. Negrete and C. Lartigue, Learning from education to communicate science as a good story, *Endeavour* 3 (2004) (28) 120-124

[9] A. Negrete, So what did you learn from the story? Science communication via narratives, VDM Verlag & Co., 2009.

[10] R. Srinivasan, Knowledge architectures for cultural narratives, *Journal of Knowledge Management* 9 (2004) (4) 65-74.

[11] A. Negrete, *Tell Me How Much Science You Can Tell*, Lambert Academic Publishing, 2014.

[12] M. Tatalovic, Science comics as tools for science education and communication: A brief, exploratory study, *Journal of Science Communication* 8 (2009) A02.

[13] J. Hosler and K. B. Boomer, Are comic books an effective way to engage non-majors in learning and appreciating science?, *CBE Life Sciences Education* 10 (2011) 3 309-317.

[14] S. McCloud, *Understanding Comics: The Invisible Art* (6th ed.), New York: Harper Perennial, 1993.

[15] C. Trent and R. Kinlaw, Comic books: An effective teaching tool, *Journal of Extension* 17 (1979) 18-23.

[16] G. L. Putnam and K. L. Yanagisako, Skin cancer comic book: Evaluation of a public educational vehicle, *Cancer Detection and Prevention* 5 (1982) (3) 349-356.

[17] M. A. El Setouhy and Rio F., Stigma reduction and improved knowledge and attitudes towards filariasis using a comic book for children, *Journal of the Egyptian Society of Parasitology* 33 (2003) (1) 55-65.

[18] L. Yuan, L. Manderson, M. S. B. Tempongko, W. Wei and A. Aiguo, The impact of educational videotapes on water contact behaviour of primary school students in the Dongting Lakes Region, China, *Tropical Medicine and International Health* 5 (2000) (8) 538-544.

[19] M. P. A. Liebman, P. M. Juárez, Cl. Leyva and A. Corona, A pilot program using Promotoras de Salud to educate farmworker families about the risks from pesticide exposure, *Journal of Agromedicine* 12 (2007) (2) 33-43.

[20] CANIEM, Producción editorial, accessed date 20-04-2015, available online at: http://www.caniem.com/.

[21] A. Malvido, Los libros: mundo e imaginación en peligro (y siete entregas más). La Jornada, 1993.

[22] D. Chun and J. Plass, Effects of multimedia annotations on vocabulary acquisition, *The Modern Language Journal* 80 (2006) (2) 183-198.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 809-814
Doi: 10.15341/mese(2333-2581)/12.02.2016/007
Academic Star Publishing Company, 2016
www.academicstar.us

Measuring Land Cover Changes Caused by Surface Mining Expansion Using Lands at Data at Camaquã Mines, Brazil

Matheus M. Pimenta[1], Fernando A. C. Cardozo[1], Rafael R. Ribeiro[2], and André C. Zingano[1]

1. Departmentof Mining Engineering, Federal University of Rio Grande do Sul, Porto Alegre, Brazil

2.DepartmentofGeodesy, Federal University of Rio Grande do Sul, Porto Alegre, Brazil

Abstract: The multi-temporal image analysis is one of the most convenient and useful ways to determine how specific attributes of a particular area have changed between two or more regular intervals, comparing aerial photographs or satellite images of the study area taken at different times. This study examined the impact of the expansion of degraded areas through the mineral production and subsequent changes in natural vegetation after leaving the area over a period of 26 years in a region affected by copper mining over a century generating environmental, social and economic impacts atCamaquã Mines, southern Brazil, using geographic information system (GIS) and remote sensing (RS) techniques. A series of Landsat images were classified by normalized difference vegetation index (NDVI) to produce three land cover maps of the region. From comparisons between these maps and areas with no vegetation cover, it was possible to quantify the variation that occurs in the landscape, identifying the evolution of changes in natural vegetation area. It has been observed that between 1985 and 1996 the degraded area has increased 8%, however, in 2011 (the last year analyzed), there was greater vegetation cover than in the first reporting period, resulting in vegetation recovery of 26% when compared to 1985.

Key words: remote sensing, GIS, mining, land cover, NDVI

1. Introduction

After the advent of the first remote sensing satellite (Landsat 1), in 1972, the preparation of accurate reports about the use and land use, changes in vegetation cover, environmental monitoring, natural resource management and urban development have become relatively simple, enabling the making of numerous studies combining field research and satellite data in many areas, such as urban and agricultural areas. In the case of inaccessible areas, the only method of obtaining data for the application of geographic information system (GIS) and remote sensing (RS) techniques in the observation of periodic changes on the surface of the Earth [1].

Although this technology has been available for many years, the use of remote sensing for monitoring of mining activities has rarely been applied, although, according to K. Koruyan et al. (2012) [2], this tool has been proven valuable in the management and planning of some aspects in the operation of mining projects.

Change detection in remote sensing is described by Singh (1989) [3] as “the process of identifying differences in the state of an objector phenomenon by observing it at different times”, determining how specific attributes of a particular area changed between woor more regular intervals, comparing aerial photographs or satellite images of the area taken at different times. In general, the detection of changes in the characteristics of the earth’s surface, according to

Corresponding author: Matheus Montes Pimenta, M.Sc. Student, research areas/interests: mining and geotechnical engineering, rock mechanics. E-mail: matheus.pimenta@ufrgs.br.

Lu et al. (2011) [4], provides the basis for a better understanding of the relationships and interactions between human and natural phenomena, assisting in the management and use of resources; and invariably this involves the application of multi-temporal image analysis.

In this case study, we have examined the impact of expansion of degraded areas for mineral production and subsequent changes in natural vegetation over a periodof 26 years in a region affected by copper surface mining for over a century, causing environmental, social and economic impacts in Minas do Camaquã, in the municipality of Caçapava do Sul, Rio Grande do Sul, Brazil (Fig. 1). Using remote sensing techniques, degraded and recovered vegetation areas post-mining activity were measured and calculated based on multispectral and sequential analysis of satellite images of normalized difference vegetation index (NDVI).

It was adopted as image selection parameter: (1) the period in which it had data availability (the Landsat 5 satellite was launched in 1984 and closed in 2013), (2) image quality that would allow the application of the vegetation index and (3) representativeness in relation to historical events in the region.

(1) 1985: Four years after mining company starts modern and mechanized operation;

(2) 1996: year of deactivation and abandonment;

(3) 2011: one year before starting ecotourism activities.

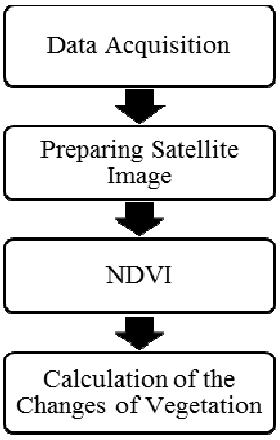


Fig. 1 Flowchart of methodology.

2. Material and Methods

In order to check the environmental impact and detect the evolution of changes in vegetation cover in an abandoned mining area, remote sensing techniques have been applied in the analysis of a Landsat time series. For the acquisition of data, the coordinates of the study area (described in Study Area topic), satellite images Landsat 5 (which has 30 meters of resolution in the bands of visible and infrared) were collected during three different periods, August 1985, June 1996 and April 2011, and then the impact coverage zones were determined. Finally, the degraded area and in particular the changes in vegetation cover were quantified.

The Fig. 1 shows a sequence of tasks applied in this study, and each step of analysis and image processing are explained in detail in the following topics.

3. Study Area

The study area is located between latitude and longitude -30.908591, -53.446582 and is part of the geological unit “Escudo Sul Rio-grandense”, Caçapava do Sul district. The copper ore discovery in the region is dated 1865 and there were several cycles of operation and decommissioning until the Second World War.

In 1942, the Brazilian Copper Company (CBC) was founded, with the participation of the State Government, the National Lamination Metals and owners and concessionaires of the mines. Its foundation arose from the need to produce strategic materials, including copper, during the war. In 1952 the Pignatari Group took control of the company, selling it to the Federal Government through the National Bank for Economic and Social Development (BNDES), and in 1975 the operation was suspended given the poor conditions of underground mining, which had reached 150 meters of depth, and the deactivation of the metallurgy that used copper produced in Minas do Camaquã. In this period, the CBC has directed its activities to geological research in order to develop the characterization of the ore and expansion of reserves,

thus allowing the implementation of the "Camaquã Expansion Project". Mining activities were resumed in 1981 and highly mechanized extraction techniques came to be used both in underground mines and in open-pit mining. In 1987, BNDES assumed the entire bank debt of the company and in 1988 the CBC was put up for auction and has not been sold to any of the companies qualified by withdrawal (the companies qualify by withdrawal? Consider redrafting this bit). As a workaround, the CBC has just been bought by its own employees, who have come to form a new company. The BomJardim SA took over the activities, paid off its debt to the BNDES, before the deadline stipulated in the Protocol of Intentions, and continued to mine copper until May 1996, when the economically viable reserves known became totally depleted [5].

4. Image Data and Processing

For this study we have used Landsat 5 satellite images, obtained at the Brazilian National Institute for Space Research (INPE) website [6]. The images were processed in ArcGis and ERDAS software. The limits of mining and degradation were determined in the time interval using digital image processing. After delimitation and selection of the study area, the vegetation index (VI) tool available on ERDAS was applied.

Fig. 2 Location of the study area.

5. Estimation of Change in the Natural Vegetation

The Vegetation Indexes (VI) are computed and calculated from the numerical value of brightness, this work will be used vegetation index (NDVI), which in addition to map also allows you to measure the quantity and condition.

The NDVI is calculated using the portions of electromagnetic energy reflected by the vegetation in the bands of red (wavelength = 0.6 micrometers) andnearinfrared (wavelength = 0.8 micrometers). It is the product of a function which takes as input parameters from the spectral bands of red and infrared. The reflectance of bands 3 (red-visible) and 4 (infrared-near) of the Landsat 5 sensor, which are determined by the following relationship:

$$\rho_{0,i} = \frac{L_{rad}*\pi}{E_{0,i}*cos\theta*d_r} \quad (1)$$

Where $\rho_{o,i}$ is the spectral reflectance in band i, d_r is the inverse square of the Earth-Sun distance in astronomical unit, $E_{0,i}$ is the average value of exoatmospheric solar irradiance in the band i expressed in $Wm^{-2}\mu m^{-1}$ (solar constant), θ the solar zenith angle (calculated from the solar elevation angle) and L_{rad} is the spectral radiance in band i in $Wm^{-2}sr^{-1}\mu m^{-1}$.

After thatwas carried out the atmospheric correction by the Dark Object Subtraction (DOS) method, using the histogram of each band to select the darkest pixel [7].

The NDVI was determined by the following relationship:

$$NDVI = \frac{\rho iv - \rho v}{\rho v + \rho v} \quad (2)$$

Where ρiv and ρv represent the reflectance bands in the infrared and red.

As a result of the application of Eq. (2), the product generated is stamped with the values of NDVI ranging within the range -1 to +1, with -1 representing total absence of vegetation and +1 maximum detected the presence of vegetation.

6. Results and Discussions

After the images were processed and generated the NDVI indexes, the cutoff of about 0.30 was set to vegetation and no vegetation. Thus, all above 0.30 was considered as vegetation and all below that was considered as no vegetation.

In Fig. 3 you can see the vegetation dynamics of change in the study area, characterized by a contraction of the same between the periods 1985 and 1996, the mine operation lifetime, and finally, expanding the vegetated area in the period 1996 to 2011, the period after deactivating the mine and abandonment.

Through analysis of NDVI index, which defines thecutat 0.30 wascalculated in the software ERDAS the vegetation pixel count (NDVI > 0.30) and degraded area (NDVI < 0.30), as the satellite has a spatial resolution of 30 meters, the area of each pixel corresponds to 900 m². The measurements of surface mine expansion and vegetation cover area changes are presented in Table1.

The Fig. 4 below shows a graph with the evolution of degraded area in the analyzed period, in which there

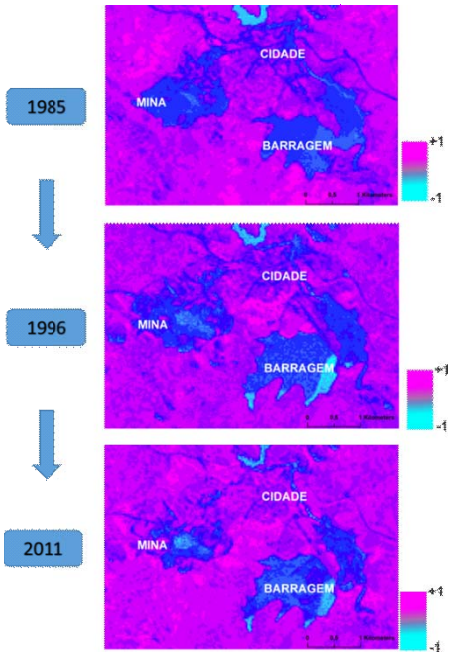


Fig. 3 An example of the land use/cover expansion and effect on vegetation between 1985 and 2011. (+1) Vegetation. (-1) No vegetation. Mine (mina), Town (cidade) and Dam (barragem).

Table 1 Expansion of mining and vegetation cover area.

Area(m²)	2011	1996	1985
Degraded	4,693,500	6,300,000	5,825,700
Vegetation	16,785,000	14,896,800	15,486,300
	DegradedArea		
Period	Variation(m²)	Cumulative(m²)	Rate(%)
1985-1996	474,300	474,300	8
1996-2011	-1,606,500	-1,132,200	-26

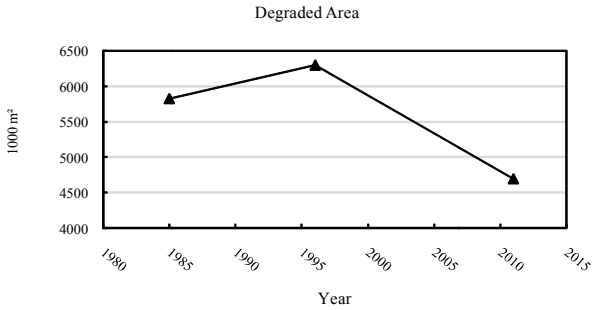


Fig. 1 Expansion of degraded area between 1996 to 2011.

is a clear recovery of the vegetation on the degraded area between the period from 1996 to 2011.

Fig. 5 shows the area corresponding to the open pit

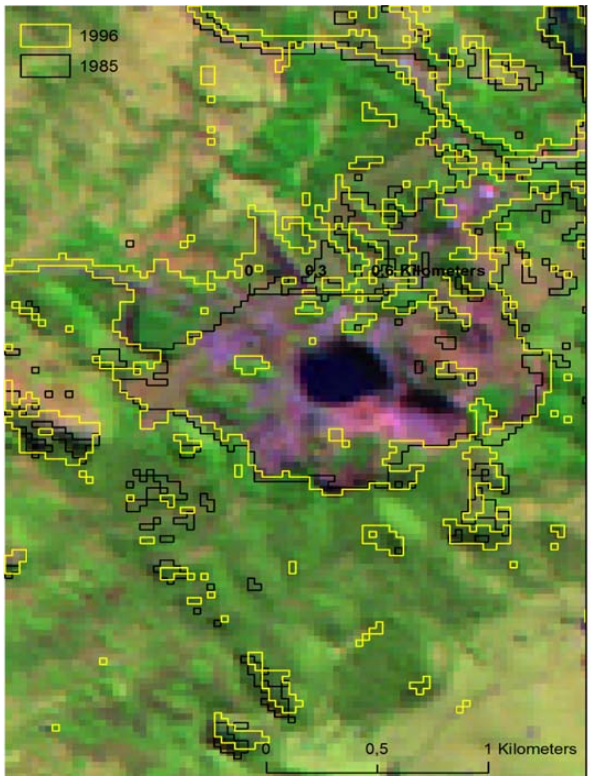


Fig. 5 An example of the expansion of mining activity between 1985 and 1996 (different colours represent mine boundaries related to the years).

mine in isolation from other structures, this analysis is the vectorization of the area marked as degraded from NDVI. This corresponds to the color composition of the year 2011 (RGB 542), in which are represented in yellow the degradation boundaries of the year 1996 and in black the boundaries of the year 1985.

7. Conclusions

A quick literature review shows that remote sensing methods can be used to classify the types of land use in apractical, economic, repetitive and large areas. Although change detection techniques have been widely used in multidisciplinary scientific studies to monitor and evaluate the impacts of natural processes and human activity on the environment, few studies using these tools have been conducted to evaluate changes in areas affected by mining activity.

In this paper, the authors presented an estimate of the expansion of the degraded area and the changes in vegetation associated with mining activity through multi-temporal analysis of the years 1985, 1996 and 2011, applying the NDVI index.

It was observed that the area without vegetation cover increased between 1985 and 1996 and that there was a great expansion of vegetation after the closure of operations and abandonment of the area in 1996, advancing over 26% of the area characterized as degraded, and in 2011 the area with greater vegetation covers the first analyzed date. Total of an area is about 113 ha. It should be noted that this data is from the area affected by mining as a whole, including the construction of the mining town (urban sprawl), tailings dam and open pit. By only analyzing the influence of the open pit region, visually it is possible to notice a big vegetable recoating.

The depletion of mineral resources has been a common event throughout world history, but neglect and impoverishment of these regions is not an inevitable consequence. The use of remote sensing and geographic information system have an increasing role in the management of mining areas. Together, they provide information and statistical data for the evaluation of habitat diversity and changing land cover while the mine is in operation, which may be used to formulate policies and guidelines for the management post-mining and in planning the closure of the mine, environmental reclamation, monitoring, characterization of the landscape and socioeconomic alternatives for rehabilitation of the area in the production system. In this study area, the municipality was adopted in 2012 ecotourism as an alternative to use the area.

As future work, we suggest (1) the classification of different types of vegetation occupying the area, for example: dense vegetation, grassland, scrub, native vegetation and exotic vegetation, etc; (2) multi-temporal analysis in stream subbasin João Dias, in order to identify changes in drought conditions and contamination of sedimentation, as it received the solid waste and liquid effluents from the treatment of copper ore since the nineteenth century until the construction of the tailings dam at the end of 1970; (3) identification of the variation in average vegetation index only in the mine pit area and (4) inclusion of images from different periods in the analysis.

Acknowledgements

The authors are grateful for funding received from the Luiz Englert Foundation (FLE), the Federal University of Rio Grande do Sul and the Department of Mining Engineering.

References

[1] B. Majumber, Land use and land cover change detection study at Sukinda Valley using remote sensing and GIS, master's thesis, National Institute of Technology Rourkela, 2010.

[2] K. Koruyan, A. Deliormanli, Z. Karaca, M. Momayes, H. Lu and E. Yalçin, Remote sensing in management of mining land and proximate habitat, *The Journal of The Southern African Institute of Mining and Metallurgy* 122 (2012) 667-672.

[3] A. Singh, Digital change detection techniques using remotely sensed data, *International Journal of Remote Sensing* 10 (1989) (6) 989-1003.

[4] D. Lu, E. Moran, S. Hetrick and G. Li, Land-use and land-cover change detection, in: Q. Weng (Ed.), *Advances in Remote Sensing: Sensors, Algorithms and Applications*, New York: CRC Press, 2011, pp. 273-290.

[5] P. Paim, Minas do Camaquã, RS – Marco da história da mineração de cobre no Brasil, in: C. Schobbenhaus et al. (Eds.), *SítiosGeológicos e Paleontológicos do Brasil*, Brasília: DNPM/CPRM/SIGEP, 2002, pp. 501-510.

[6] Image Catalog (CDI), Brazilian National Institute for Space Research (INPE), October 10, 2015, available online at: http://www.dgi.inpe.br/CDSR.

[7] S. Gürtler, J. Espihanio, A. Luiz and A. Formaggio, Electronic spreadsheet to acquire the reflectance from the TM and ETM+ Landsat images, *Brazilian Journal of Cartography* 57 (2005) (2) 162-167.

Modern Environmental Science and Engineering (ISSN 2333-2581)
December 2016, Volume 2, No. 12, pp. 815-821
Doi: 10.15341/mese(2333-2581)/12.02.2016/008
Academic Star Publishing Company, 2016
www.academicstar.us

Citizen Science a Tool for Community Engagement in Parks with an Urban Dominating Landscapes in Puerto Rico

Yogani Govender[1], Sandra Faría[2], Astrid Maldonado[2], Jean Manuel Sandoval[2], Carlos Báez Torres[2], and Rubén Estremera-Jiménez[3]

1. Inter American Universityof Puerto Rico, Metropolitian Campus, Puerto Rico

2. Para la Naturaleza, San Juan, Puerto Rico

3. University of Puerto Rico, Rio Piedras Campus, Puerto Rico

Abstract: With a population of 3.5 million on an island of 100 miles long and in severe economic crisis partners for the conservation of biodiversity is crucial for the sustainability of urban natural protected areas (NPA surrounded by large population centers, IUCN). The Conservation Trust of Puerto Rico (CTPR) is using citizen science (CS) an informal science education method to engage citizens in nature. While the conventional model for CS is a participant attending a workshop or training session, learn standard methodologies to measure and assess species, habitats and ecosystems from a scientist and then go off to collect data on their own and share data with the scientist, the CTPR propose an alternative model that includes the scientist with citizens, throughout the spatial and temporal long-term data collection. In this model, the citizens are mentored by the scientists or scientist assistant to pass through the different phase of the Informal Science Education model (contributory, collaborative, co-created). The main goal is to enable the citizens to develop the skills of scientific inquiry and to address environmental concerns within their community. Of the 1300 participants 19 have developed community based projects to better understand their environment and the impacts of urban development. The co-creator participants have used three levels of communication to disseminate findings of biodiversity in NPA along an urban gradient. The citizen science research projects conclude that urban protected areas play an important functional role in the watershed.

Key words: citizen science, urban dominating landscapes, natural protected areas

1. Introduction

For decades' governments and conservation organizations around the global are using environmental education to inform the public about the value of biodiversity and the ecosystems services provided by Natural Protected Areas (NPA). The educational experiences are mechanisms used to increase visitor's knowledge and reduce anthropogenic impacts within the NPA [1, 2]. The educational strategies and programs have included informative videos, conferences, self-guided, nature walks and tours to educate the public about the natural spaces, the species and ecosystems they contained, the threats facing them and what actions are taking place at local scales to protect them. In the early days of the Yellow Stone National Park for example, educational programs were initiated to better protect the park, its wildlife and its resources. Park programs, exhibits and literature educated visitors about the park's fragile ecosystem.

As early as 1920's, this NPA introduced citizen science to collected bird data within the Yellowstone National Park, park naturalist Milton Skinner completed the first Yellowstone Christmas Bird Count

Corresponding author: Yogani Govender, Ph.D., research areas/interests: ecology, citizen science, climate change. E-mail: yygovender@metro.inter.edu.

and continues today [3]. Today the educational programs involving citizens is wide ranging, from recycling programs to monitoring disease in wolves [4]. The educational programs at U.S. NPA and around the globe have evolved to include citizen science programs for the integration of research and hands-on experiences, bringing together different skills sets to find new solutions and deeper visitor connection with natural resources and the NPA [5, 6]. In Puerto Rico, however educational programs until recently remained conventional in NPA.

Puerto Rico is an island 111 miles long by 39.5 miles wide, in the Caribbean (Fig. 1) experiencing rapid urban development in both metropolitan and rural areas, resulting in loss of biodiversity, habitat loss and major environmental problems [7, 8], such as the impacts to main sources of freshwater from the karst regions of Puerto Rico [9]. The Rio Grande of Manatí Watershed (Fig. 1) is found within the northern Karst region, where there are increased proposals for urban developments in its nine municipalities: Orocovis, Barranquitas, Morovis, Ciales, Florida, Jayuya, Corozal, Manatí y Barceloneta. During focus group meetings held with volunteer leaders and watershed stakeholders, concerns included loss of biodiversity within the region, impacts to unique ecosystems (caves and underground rivers), reduced water quality, laws that do not take into account the importance of the karst, uncontrolled land use, and deterioration of local roads. Non-profit organizations of the area have engaged in efforts to increase public awareness on these impacts through dissemination of information, but citizens feel that they do not have the full spectrum of scientific knowledge or the tools to address the issues that are significant to them. Research shows that engaging people directly with research helps them become comfortable with tools and practice of science [10].

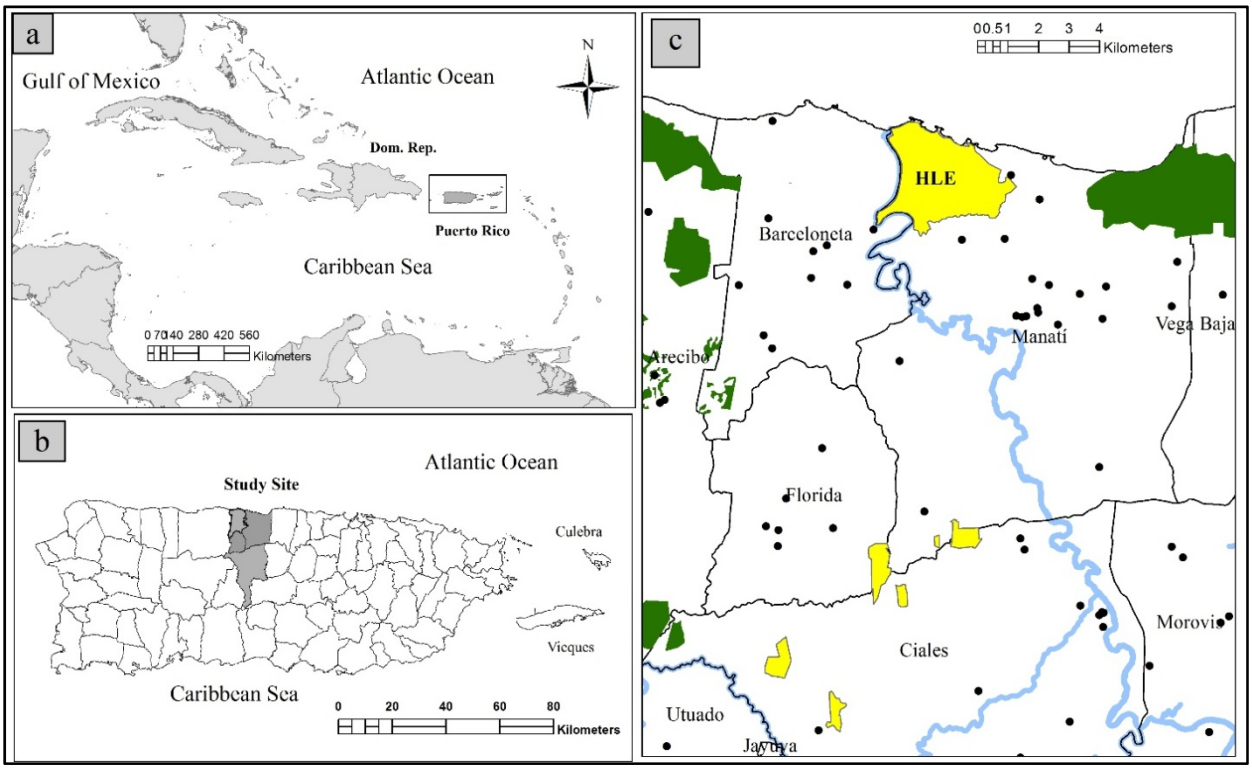


Fig. 1 Map Showing a) Location of Puerto Rico in the Caribbean, b) Study site in the northern coast of Puerto Rico c) Landscape of the Rio Grande of Manatí Watershed. Yellow polygons show natural protected areas managed by Para la Naturaleza and green polygons showing state managed natural protected areas. Black dots represent schools within the watershed as an indicator of urban development.

The Millennium Ecosystems Assessment (2005) shows that citizens who become significant actors in their environments play important roles in decisions linked to the use of those areas. While Sheedy (2008) state that citizens knowledgeable of the areas that they live in develop a sense of ownership and engage in behaviors, initiatives, and processes that address their neighborhood affairs [11].

The Conservation Trust of Puerto Rico (CTPR) established in 1970 currently owns and manages Natural Protected Areas which is 1% of the 16% of lands under protection and conservation in Puerto Rico. Their mission is to protect and conserve ecological and culturally important natural areas where they use educational guided tours, summer workshops and school gardens as a tool to educate about 60,000 visitors annual about species, ecosystems and their protection in Puerto Rico. With immense pressure for development in the past decades within sensitive cultural and ecological areas and little public advocacy, the CTPR decided to explore Citizen Science as an option to deeply engage participants in conservation actions. At first through a National Science Foundation funded project, they invited citizens to document with scientist the biodiversity of a Natural Protected Area of Hacienda La Esperanza (Fig, 1). The purpose of the project, in the municipality of Manatí, was a means to create stewards of nature that not only receive facts through tours but carry out actions to participate in the protection and conservation in nature. The project was highly successful with the development citizen science hands on toolkits and where some 2,322 participants actively collected scientific data and 48% whom returned to the project. Of these participants many have become volunteer leaders of the CTPR and now actively advocate for nature protection and conservation.

Based on the success of the first project within a NPA and using the framework developed by Bonney et al. (2009) for engaging citizens in conservation of nature through informal science education (ISE) the research team present using citizen science as an educational model to engage citizens in learning and implementing scientific process as they pass through the three levels of the ISE model-contributory, collaborators and co-creators. In the contributory phase participants mostly collect and record data, in the collaborator phase participants collect data, analyze samples and data and in the co-creator phase participants choose and define questions of research, gather resources and information, develop hypothesis or explanations, design data collections methodologies, collect data, analyze samples and data, interpret data and draw conclusions, disseminate conclusions and translate results into actions.

In five ecological research projects the impacts of urbanization along the Rio Grande de Manatí (Fig. 1) was evaluated by comparing biodiversity and ecosystems functions and processes within NPA and in areas surrounded by or close to urban development. The research project on Bats, evaluated the impact of urban development on bat diversity, the archaeological project investigated how humans used the river and the forest for resources and modified the local environments, the shrimps and crabs project looked at the water quality along an urban gradient comparing rivers in NPA with urban areas, the birds and forest project investigated forest fragmentation due to urban development and the coastal process project looked at the changes to geomorphological processes due to urban development along the banks of the river. Besides collecting baseline data on biodiversity and ecosystem process the projects provided opportunities to participants to 1) gain scientific knowledge with a well renown researcher 2) develop community based citizen science projects that is relevant to communities surrounding NPA and 3) to develop skills to communicate scientific results from their project to the wider community. Researchers in each project encouraged all participants to repeat field activities and invited them to develop their community citizen science projects after they developed sufficient skills

and knowledge about the specific ecological theme.

Over 600 activities (workshops, field trips and laboratory) were provided to transform citizens towards the three levels of ISE participation. All participants were given the opportunity to learn scientific methodology and specific scientific information about biodiversity through democratic bilateral learning and teaching processes in field and laboratories. The experiences in workshops allowed scientists to provide repeat participants in depth explanations about the methods and equipment used to collect biodiversity and ecosystem data in NPA and urban areas, creating an environment for questions and answers so that doubts and uncertainty is reduced when in the field. In the field, researchers used various teaching techniques to engage the participant so they transformed to collaborators and co-creators.

The demographic profile of all subjects participating in the activities of the five investigations was analyzed. There was a participation of 1,337 subjects in five projects, 548 (59%) were male and 789 (41%) female. Participation was diverse by age from children, youth, young adults and adults. Majority of participants (56%) were grouped into categories of young people (14 to 18) and young adults (19-28 years) (Table 1).

The profile of the general population of the project volunteers in the areas of gender and age profile is relatively similar to co-creators and collaborators. Of the 1,337 total participants five participants reached collaborator phase and fourteen reached co-creator phase. There is a higher percent of people over 44 years in the co-creators group (32%), when compared with the general population.

Table 1 Age distribution of participants in citizen science in urban dominated landscapes.

Age (Years)	Participants N = 1125		Co-creators/collaborators n=19	
	f	%	f	%
1 to13	51	5	2	11
14 to18	178	16	4	21
19 to23	322	29	1	5
24 to 28	129	11	5	26
29 to33	62	6	0	0
34 to38	64	6	0	0
39 to 43	77	7	1	5
> 44	242	22	6	32

During the past two years' the 7 co-creator's projects were completed and 6 are still in progress and 1 dropout. Each co-creator worked with a scientist mentor to develop research questions of their interest, write a proposal and implement their project in their community. They were asked to actively disseminate the findings of their projects within various settings using different media from schools, community meetings, open house, universities, symposia and congresses. Each co-creator had to involve volunteers in their projects and document the hours they contributed. For the past year co-creator projects have contributed 1,098 hours in volunteer activities with members of the community in urban dominated landscapes both with NPA and in urban areas. Each project below describes the co-creator's projects and achievements

Daniel Rivera Luis Collazo: *Monitoring water quality in the Rio de Bauta*

Daniel Luis Rivera completed the project monitoring water quality in the Rio de Bauta, Orocovis. He was mentored by Dr. Concepción Rodríguez Fourquet for scientific rigor and methods[1].

Jose Figueroa Pesquera:

This co-creator together with Dr. Concepción Rodríguez Fourquet successfully conducted the filming of a documentary local ecological knowledge about the shrimping and the importance of conservation of the river Torre Negro in Ciales. Consequently, published in Facebook, Twitter and YouTube pages for the Conservation Trust as river fishing in Puerto Rico: tradition and wisdom[2].

[1] https://www.facebook.com/Ciudadano.Cientifico.Orocovis?fref=ts.

[2] https://youtu.be/vNWvR9C8x-Y.

Sandra Berlingeri, Manuel A. Garcia Vega, Manuel A. Garcia Berlingeri, Jose F. Garcia Berlingeri: Water quality monitoring project in river Indio, Morovis

The family Garcia Berlingeri mentored by Dr. Concepción Rodríguez Fourquetcompleted the water quality monitoring project in river Indio, Morovis. The results surprised the team to co-creators where they found waste water treatment plant did not contribute to high levels of *E. coli* found in the river and they attribute this to poor management septic tanks of their neighbors.

Kimberly Melendez Rodriguez: Monitoring birds in the State Forest of Monte Choca, Corozal

This 16-year-old co-creator working with scientist Jose Salguero Faría developed a bird census project to monitor bird in the State Forest of Monte Choca. In May 2015 in recognition of the work completed by Kimberly she was featured in the website "EnVuelo" in a documentary.

Ricardo Rodríguez Vélez and Laura Rodríguez Rodríguez: Bird census and educational project at Cueva Escalera, Florida. This team together with scientist Jose Salguero Faría developed a bird census project at Cueva Escalera.

Gladys Valentin Gonzalez: Effects of cyclonic systems that impact the north and west beaches of Puerto Rico. This co-creator mentored by Dr. Maritza Barreto Orta presented findings on April 21-25, 2015 at the annual meeting of the American Association of Geographers in Chicago, Illinois[3].

Jean Carlos Colón Bergollo: Comparing changes in beach profiles in two beaches of Culebra, Puerto Rico. Together with Dr. Maritza Barreto Orta presented findings of his project was shared with peers at the annual meeting of the American Association of Geographers in Chicago, Illinois[4].

Valeria Torres Lopez: Geomorphological changes of the beach at Ocean Park

This co-creator together with her mentor Maritza Barreto Orta shared findings in April 21-25, 2015 at the annual meeting of the American Association of Geographers in Chicago, Illinois[5].

Venus Andrea Hernandez Paez: Identify bat species present in the Northeast Ecological Corridor. This 14-year-old together with mentor Dr. Armando Rodriguez Duran have taken demystifying bats to the community. In October 28, 2015, she presented her work at the North American Symposium on Bat Research (NASBR) in Monterey, California and was invited on November 6, 2015 to offering an educational talk about bats in the office Wildlife Refuge of Vieques[6]. *Dereck González Pérez*: Identify bat species present in the Miraflores, Arecibo. Also a 14-year-old accompanied by his mother and mentor Dr. Armando Rodriguez Duran monitors using ANABAT the different bat species present in the Miraflores district of Arecibo located in the Northern Karts of Puerto Rico. He has contributed 133.50 volunteer hours since July 2015. On 28 October 2015, he presented results at the North American Symposium on Bat Research (NASBR) in Monterey, California.

Hector Rivera Claudio: Exploring the history and use of agricultural terraces in the Protected Natural Area El Cuco. Hector is working with his mentor Dr. Isabel Rivera Collazo. On 15 April 2015, he presented his Citizen Science at the conference of the Society for American Archaeology (SAA), California. He was also invited to publish his findings in the Journal American Archaeology. His article is currently in press.

Miguel Diaz Diaz: Effects of geomorphological changes on archeological deposits at Tierras Nuevas within the Hacienda la Esperanza. Used the methods learned during two different research projects within this citizen science project and combined them. He is mentored by two scientists Dr. Maritza Barreto Orta

[3] https://drive.google.com/file/d/0BwTAHd5SeNtWNXBCdFNBekxCZmM/view.

[4] https://drive.google.com/a/ciudadanocientifico.org/file/d/0BwTAHd5SeNtWX29LRVlzbG1UbGM/view?usp=sharing.

[5] https://drive.google.com/open?id=0BwTAHd5SeNtWb0JwVDRSUXRyYk0.

[6] https://www.facebook.com/photo.php?fbid=556459991178149&set=a.324874434336707.1073741828.100004424598058&type=3&theater.

and Dr. Isabel Rivera and has shared his results with peers on April 15, 2015 at the conference of the Society for American Archaeology (SAA), California and on April 20, 2015 at the Geological Society of America Conference in Chicago, Illinois.

During the progression of the citizen science project co-creators started communicating project finding is various forums. Initially collaborators and co-creators started teaching first time participants field activities including methodology to collect data, data entry and answering questions. As they grew with knowledge and confidence collaborators and co-creators accompanied researcher to local symposiums and community based conservation activities and science fairs. At the co-creator phase, once they developed their community based projects participants began presenting national and international forums with academic peers and to audiences who were experts in the respective ecological themes. The various communication mechanisms were categorized into 3 levels (1) Divulge (share with general public) (2) Diffusion (share with target audience schools, community conservation groups) and (3) Dissemination (share with other scientists in the field: experts) (Fig. 2).

The ability of co-creators to effectively communicate about their projects served as a bench mark to evaluate attitude of participants towards science and towards conservation. Majority (53%) of the activities where the co-creators presented targeted general communities to share their experiences but also to invite communities to become active in conservation of biodiversity and ecosystems. The success of the techniques used to educate citizens scientist in scientific methods, knowledge and skills is reflected on the ability of co-creators to present at national and international congresses with experts in the field (40%). Citizen scientists managed to impact community surrounding the urban natural protected areas through various media (Fig. 2).

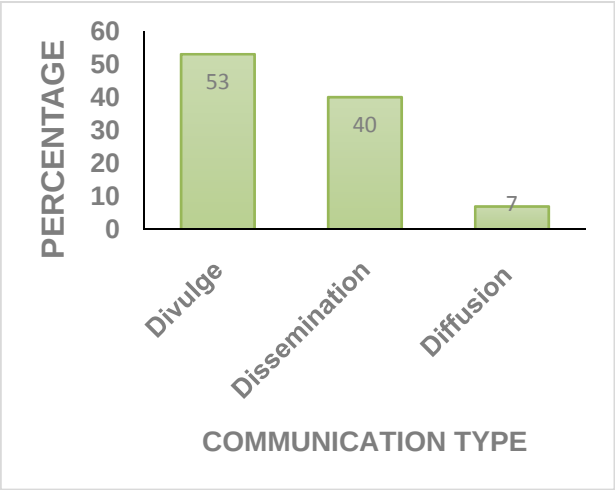


Fig. 2 Diverse means of communication used by participants in citizen science community projects.

2. Conclusions

Citizen scientists are important partners for NPA managers to engage communities to protect and conserve biodiversity and ecosystem processes. Repeat participation, bilateral communication during data collection and data analyses with a scientist is the cornerstone of engaging community members to develop science projects that is relevant to their social, economic and cultural context. Communicating experiences and results through diverse mechanisms for diverse audiences effectively educate about the impacts of urban development on biodiversity and ecosystems in NPA. The types of projects developed by citizen's scientists, the rigor of scientific process and time they dedicated to learn about their urban dominated landscape indicates the value of using citizen science as an educational tool in conservation.

Acknowledgements

This project was funded by the National Science Foundation (Grant # 128832) and logistical support was provided by Para la Naturaleza. Field activities were provided by individual researchers Dr. A. Rodriguez (Bats), Dr. C. Rodriguez-Fourquet (Shrimps and Crabs), Dr. I. Rivera-Callazo (Archeology), Dr. M. Barreto-Orta (Coastal Processes), and Mr. J. Salguero-Faría (Birds and Forests). Further the authors would like to thank all volunteers, volunteer leaders,

student assistants and co-creator/collaborator participants who have been dedicated to engaging citizens along the Rio Grande de Manatí.

References

[1] Jeffrey L. Marion and Scott E. Reid, Minimizing visitor impacts to protected areas: The efficacy of low impact education programs, *Journal of Sustainable Tourism* 15 (2007) 1.

[2] MillenniumEcosystems Assessment, Ecosystems and human well-being, World Resources Institute Washington, D.C.,2005, available online at:http://www.maweb.org/documents/document.358.aspx.pdf.

[3] McEneaney Terry, Yellowstone Christmas bird counts of the twentieth century Christmas bird counts continue in Yellowstone — A tradition both scientific and social, *Yellowstone Science* 9 (2001) 1.

[4] Ranger Program NPS, retrieved August 2016, available online at: http://www.ohranger.com/yellowstone/preserving-park.

[5] S. Weber, Engagement, education, and expectations—The future of parks and protected areas, in: *Proceedings of the 2015 George Wright Society Conference on Parks, Protected Areas, and Cultural Sites*, Hancock, Michigan: George Wright Society, 2016.

[6] J. C. Tweddle, L. D. Robinson, M. J. O. Pocock and H. E. Roy, Guide to citizen science: developing, implementing and evaluating citizen science to study biodiversity and the environment in the UK, Natural History Museum and NERC Centre for Ecology & Hydrology forUK-EOF, available online at: http://www.ukeof.org.u, 2012.

[7] Y. Govender and J. R. Thomlison, Changes in landuse/landcover affect distribution and habitat of the land crab, Cardisomaguanhumi (Gecarcinidae, Decapoda) in two estuaries, Puerto Rico, *Caribbean Journal of Science*.

[8] S. Martinuzzi, W. A. Gould and O. M. Ramos-González, Land development, land use, and urban sprawl in Puerto Rico integrating remote sensing and population census data, *Landscape and Urban Planning* 79 (2007) 288-297.

[9] T. Kennaway and E. H. Helmer, The forest types and ages cleared from land development in Puerto Rico, *GIS Science & Remote Sensing* 44 (2007) (4) 356-382.

[10] M. Fenichel and H. A. Schweingruber, *Surrounded by Science: Learning Science in Informal Environments*, Washington, D.C., 2010.

[11] A. Sheedy, *Handbook into Citizen Engagement: Beyond Consultation*, Canadian Policy Research Networks Inc., 2008.