



# The Effect of Land Use on Isotope Signatures of the Detritus Pathway in an Urban Wetland System

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**Abstract** Land use may be the anthropogenic alteration with the greatest effect on ecosystem dynamics. In aquatic systems, food web pathways are highly influenced by the land use of surrounding areas, leading to different responses to the role of detritus in aquatic food web pathways. We studied the influence of land use on benthic isotopic signatures in Xochimilco, a shallow, tropical high-elevation wetland impacted by a mix of rural and urban activities, such as agriculture, housing, tourism and mixed zones. We obtained carbon ( $\delta^{13}\text{C}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotope signatures in benthic organic matter (BOM), suspended organic matter (SOM) and *Chironomus* sp. The results for  $\delta^{15}\text{N}$  values split Xochimilco into two regions, dominated by urban or rural activities. The values of the  $\delta^{13}\text{C}$  signatures showed several differences among the zones, but without a clear pattern related to any land use. Spatial analyses showed high heterogeneity within the canals for SOM and chironomid isotope signatures, whereas the sediment values were more homogenous. This can be explained by the contribution of SOM to chironomid signatures (>96 %) calculated using mixing models. These findings suggest that land uses have different influences on carbon and nitrogen isotope signatures, affecting benthic food web pathways.

**Keywords** Isotopes · Land use · Detritus · Urban wetland · Chironomids

## Introduction

Spatial heterogeneity directly affects food web structure within aquatic ecosystems (DeAngelis et al. 1989; Polis et al. 1996, 1997), and land use is one of the main sources of this heterogeneity. The incorporation of different types of terrestrial components into water from different land uses can modify the type of sediments and the amount of nutrients (Middelburg and Nieuwenhuize 1998), thus affecting the food web of aquatic systems (Deegan and Garritt 1997; Allan 2004; Carlier et al. 2009). These changes in the food web can explain the values of isotopic signatures at different levels of the food web in heterogeneous systems (Zambrano et al. 2009).

The understanding of the aquatic food web structure has increased since isotope signatures have been developed in recent decades. Isotope signatures help to determine food web paths and organic matter sources (Vander Zanden and Rasmussen 1999; Fry 2006). The most-used isotope signatures are carbon ( $\delta^{13}\text{C}$ ), which provides information about the origin of the source, and nitrogen ( $\delta^{15}\text{N}$ ), which indicates the trophic position of the organism (Peterson 1987; McCutchan et al. 2003). The analysis of both signatures helps to elucidate the origin of the source of the organic matter in a particular aquatic system. For example, isotope signatures from allochthonous matter should have values similar to those of the primary producers of the surrounding area (Bird et al. 1992), whereas matter coming from agricultural areas will present a mixture of the isotopic signatures of the crops and fertilizers used in the region (Kellman and Marcel 2003).

In addition to allochthonous matter, biogeochemical processes also have a direct influence on the isotopic signatures within aquatic systems. Microbial activity may lead to the depletion of nitrogen isotopic values as a consequence of methanogenic and cyanobacteria metabolism (France and Schlaepfer 2000; Kohzu et al. 2004). Also, carbon and nitrogen signatures may change according to the structure and

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dynamics of the phytoplankton community (Smetacek and Hendrikson 1979), ecosystem productivity (Gu et al. 1996) or trophic status (Gu 2009). Finally, isotope signatures of suspended organic matter (SOM) and benthic organic matter (BOM, also termed sedimentary organic matter) may have a mutual influence through sedimentary-resuspension processes (Cornett et al. 1994; Bloesch 1995).

In lakes and rivers, matter flows through pelagic and benthic pathways. The pelagic path is defined by the linkage between producers (algae) and consumers (zooplankton; Wetzel 1983; Scheffer 1998). In the benthic pathways, the dominant relationship occurs between detritus (benthic organic matter, suspended organic matter and/or periphyton, which can also be considered to be part of detritus) and detritivores (invertebrates such as chironomids; Odum and de la Cruz 1963; Rich and Wetzel 1978; Scheffer 1998). The proportion of energy flowing through these pathways depends, in part, on the trophic status of the system (Gu et al. 2004). The influence of benthic pathways is greater in eutrophic systems than in oligotrophic systems, in which pelagic pathways dominate (Vadeboncoeur et al. 2002). In both, oligotrophic and eutrophic systems, the matter contained on detritus is incorporated into food webs through benthic primary consumers.

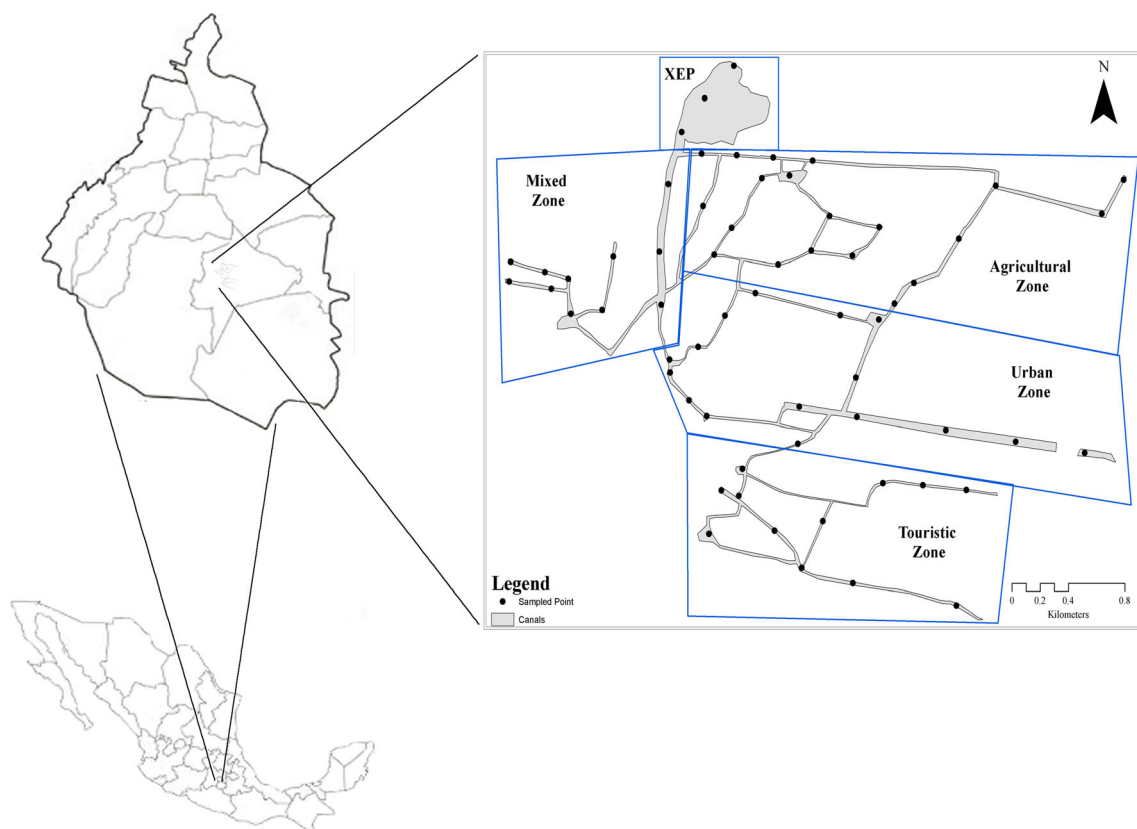
In most aquatic systems, an important group of primary consumers of detritus are chironomid larvae (Diptera) (Ferrington et al. 2008); these organisms play a key role as

energy recyclers in the water column and sediments of lakes (Pinder 1986; Ferrington et al. 2008). Moreover, chironomids can be used as markers due to their long lifetime and low mobility, integrating diverse biological processes (Lindergaard 1995). Therefore, chironomid larvae can be useful for understanding the local effects of landscape on the detritus pathway in heterogeneous or regionalized ecosystems.

Our goal is to understand the influence of landscape on the isotope signatures of the base of the food web in the detritus pathway within a highly heterogeneous and regionalized system. We determined the carbon and nitrogen isotopic signatures of benthic organic matter (BOM), suspended organic matter (SOM) and *Chironomus* sp. within an urban wetland with different land use zones, with human activities including agriculture, housing, tourism and conservation parks. We contrasted the values of each isotopic signature among the variables sampled and among the zones of the urban wetland.

## Methods

Xochimilco wetland is part of the Mexico Valley (Fig. 1), a hydrological closed formation (artificially drained) with an area of 9,600 km<sup>2</sup> (Ezcurra et al. 2006). The wetland is a shallow (Avg=1 m depth), tropical and high-elevation system harboring approximately 140 species of vertebrates, including



**Fig. 1** Xochimilco wetland zones and sampled points

migratory birds. It also hosts endemic species, such as the axolotl (*Ambystoma mexicanum*), crayfish (*Cambarellus montezumae*) and the silverside fish (*Menidia humboldtiana*; Zambrano et al. 2009). The aquatic system has been altered since pre-Hispanic times, when the wetland was modified to produce a series of canals surrounding rectangular islands called *chinampas* where traditional agriculture is still conducted (Armillas 1971). The aquatic system has since been altered; currently, most of the water supply comes from one treatment plant discharging at several locations, generating a very slow water flow to the north of the wetland (Fig. 1). The wetland suffers also from illegal discharges of sewage, exotic fish introductions and the slow but continuous replacement of traditional agriculture with greenhouses (Zambrano et al. 2009; Merlín-Urbe et al. 2012).

A wetland such as Xochimilco is ideal for understanding the relationship between land use and different pathways in aquatic food webs. Xochimilco land use is highly diverse, including historical human disturbance and heavy urban pressure continuing to the present (Terrones 2006; Zambrano et al. 2009; Merlín-Urbe et al. 2012). These land uses have generated different conditions along Xochimilco, which can be divided into zones based on Zambrano et al. (2009) and López-López et al. (2010) as follows: Agricultural Zone (a) – traditional agriculture zone where fertilizers are not used and urbanized areas are not present; Urban Zone (b) – primarily a residential zone, with scattered small areas of *chinampas* and greenhouses; Touristic Zone (c) – fully urbanized, with tourism and greenhouses as the principal activities; Mixed Zone (d) primarily agricultural, with significant portions occupied by urban areas; Park Zone (e) – wetland within Xochimilco Ecological Park (XEP; Fig. 1).

We sampled benthic organic matter (BOM), suspended organic matter (SOM) and chironomids at 62 sites (20 Agricultural; 15 Urban; 13 Touristic; 11 Mixed and 3 in the XEP) from October to December of 2008 (Fig. 1). As previous research shows that there are no significant seasonal differences in isotope signatures in most of the organisms (Zambrano et al. 2010a), we considered this set of samples sufficient to describe the dynamics along the course of a year. Samples were collected at least 200 m apart based on previous research using autocorrelation analysis (Contreras Ruiz Esparza 2012). Many samples sites were located at the intersection of two or more canals and/or in places where aquatic vegetation occurred.

Xochimilco sediment is mostly composed of silts (49.9 %) and clays (21.9 %), with minor concentrations of sand and vegetable matter (28.2 % combined; Fernández-Rendon and Barrera-Escorcia 2013). BOM was obtained from the superficial sediment, which was sampled using an Ekman dredge. We used only the upper sediment layer to a depth of two cm (Murase and Sakamoto 2000). To obtain SOM, water samples were collected at the center of the canal at a depth of 20 cm.

We sampled with the same dredge at seven points (11.3 %) along the entire system to find chironomids in sediments, but we were not successful. As a consequence, all chironomids were extracted by hand from the roots of hyacinth plants, which were normally free of macroalgae or periphyton. Previous taxonomical studies found only one species, *Chironomus plumosus* (Santacruz Barrera 2011); therefore, we considered the total of the collected organisms as this species because it appears to be the dominant one. All the samples were taken to the laboratory and preserved at a temperature below  $-4^{\circ}\text{C}$  for further processing and analysis.

To obtain BOM isotope signatures, we used one sample per site. The sediment was sieved (mesh size=1 mm) to remove large particles such as leaves, stones or other debris and dried at  $50^{\circ}\text{C}$  for 48 h. Afterwards, the sediments were pulverized in a mortar to obtain a sample of 9 mg and were then encapsulated in tin capsules.

To obtain SOM isotopic signatures, we used one water sample per site. Each water sample was passed through a filter (150  $\mu\text{m}$ ) to remove zooplankton and macrodetritus. Between 200 and 500 ml of each water sample was subsequently vacuum-filtered at low pressure (8 lb) until an APFF glass fiber filter (Merck Millipore, Billerica, Massachusetts, USA) became saturated. The resulting samples were composed of debris and phytoplankton. We considered these samples to be SOM (Kendall et al. 2001; Gu et al. 2011; Lee et al. 2013). The 62 filters were dried at  $50^{\circ}\text{C}$  for 48 h and then encapsulated. The same process was performed for 62 chironomid samples that were pulverized and dried before being encapsulated.

A set of 5 subsamples of sediments and filters (8 % of the total points sampled) were acidified and treated with the acid fumigation method to remove inorganic carbon (UC Davis 2008). The samples were moistened with drops of distilled water and placed in a desiccator with 500 ml of HCl solution (12 N) for 12 h. These samples were then processed as described above (UC Davis 2008) and used to determine the proportions of inorganic and organic carbon of BOM and SOM. The average of the difference was used to standardize the remaining samples. The samples were sent to the stable isotope laboratory at UC Davis for isotopic analysis performed using a mass spectrophotometer (Europa Scientific ANCA-HYDRA 20/20).

To determine the proportion of contribution of BOM and SOM to the isotopic signature of chironomids, a Bayesian mixing model was used with the improved version of MixSir 1.0.4 software (Semmens and Moore 2008; Semmens et al. 2009). Mixing models offer a unique mixed solution with dual isotopes (C and N) of three or fewer potential sources (Moore and Semmens 2008; Newsome et al. 2012), such as BOM and SOM in this study. We analyzed the consumer (chironomids) – source (SOM and BOM) relation by separating isotopes values

**Table 1** Percentage of contribution of suspended organic matter (SOM) and benthic organic matter (BOM) on chironomids isotopes signatures split it by zone. Results are showing the number of posterior draws, duplicate draws and MIR value as recommend Semmens and Moore (2008)

	SOM	BOM	Posterior draws	Duplicate draw	MIR
Agricultural	0.99	0.01	5,537	0	0.0003
Mixed	0.983	0.017	12,917	0	0.00001
XEP	0.04	0.96	31,105	0	5.71E-05
Turistic	0.986	0.014	10,521	0	0.00001
Urban	0.992	0.008	6,037	0	0.0003

for each zone in an attempt to identify differences in chironomid feeding proportions.

For a better approximation of the consumer – source proportion, the mean and standard variation of the source fraction are necessary (Moore and Semmens 2008; Semmens and Moore 2008). We used a fraction mean of 0.3 with an SD of 0.14‰ for carbon (McCutchan et al. 2003); and a mean of 0.53 and SD of 0.74‰ for nitrogen (Vanderklift and Ponsard 2003). Because there is no previous information on the stomach contents of chironomids in Xochimilco, we used the uninformative model with 1,000 draws, reporting the results as suggested by Semmens and Moore (2008).

To evaluate the potential relationship between BOM and SOM, a Spearman rank correlation was performed. Additionally, we used a non-parametric Kruskal-Wallis ANOVA to test for differences of isotope signatures among the zones.

To generate a map with the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotope signatures of BOM, SOM and chironomids throughout the aquatic system, we interpolated the signature values at each sample point with the Inverse Distance Weighting (IDW) method (Kravchenko 2003) using ArcGIS 8.1. The base map delimited each Xochimilco canal with a polygon, which was created based on a satellite photograph (Quickbird image, 60 cm resolution, CENAPRED, 2007) using ESRI ArcGIS 8.1. We assumed that the influence of one station decreased linearly with the distance between sampled points within 750 m and/or five points of influence. A power of two was used to represent the influence of this distance based on smoothness as a decision criterion. This interpolation technique has been useful in an aquatic system analyses in previous studies of the area (Zambrano et al. 2009; Contreras Ruiz Esparza 2012).

## Results

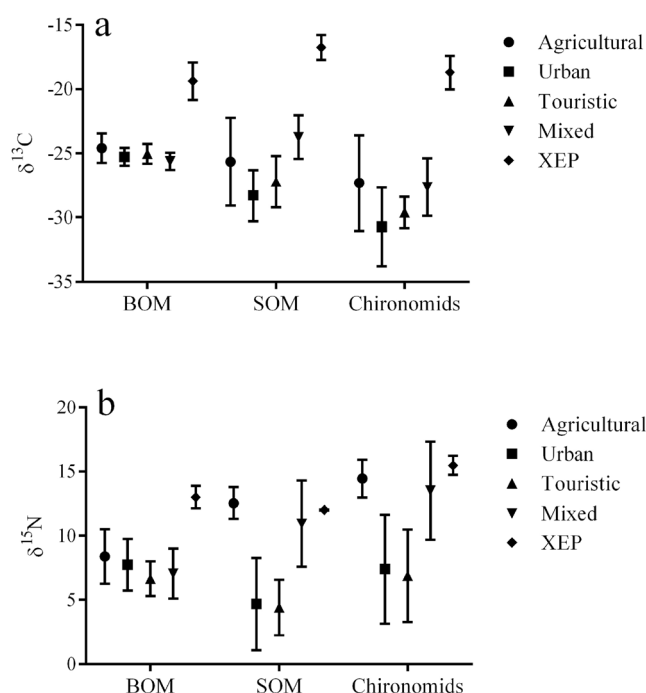
Sediment presented the highest average values of  $\delta^{13}\text{C}$  ( $-24.6$ ,  $\text{SD}\pm 1.82\text{‰}$ ) and the lowest values of  $\delta^{15}\text{N}$  ( $8.0$ ,  $\text{SD}\pm 2.3\text{‰}$ ). Chironomids showed the lowest isotopic signatures of  $\delta^{13}\text{C}$  ( $-27.77$ ,  $\text{SD}\pm 4.45\text{‰}$ ) and the highest values of  $\delta^{15}\text{N}$  ( $11.13$ ,  $\text{SD}\pm 4.75\text{‰}$ ). SOM had intermediate values of both  $\delta^{13}\text{C}$  ( $-25.9$ ,  $\text{SD}\pm 3.84\text{‰}$ ) and  $\delta^{15}\text{N}$  ( $8.4$ ,  $\text{SD}\pm 4.6\text{‰}$ ) isotopes. The  $\delta^{13}\text{C}$  signature of BOM showed no significant correlation with SOM  $\delta^{13}\text{C}$  ( $R=0.22$ ,  $p>0.05$ ). However, the  $\delta^{15}\text{N}$  values

showed a significant but weak correlation between SOM and BOM ( $0.40$ ,  $p\leq 0.05$ ).

The mixing models showed that SOM contributes more than 98 % of the chironomid isotope signature in all zones except for the Ecological Park (XEP). In contrast, BOM in XEP contributes 96 % of the chironomid isotope signature (Table 1).

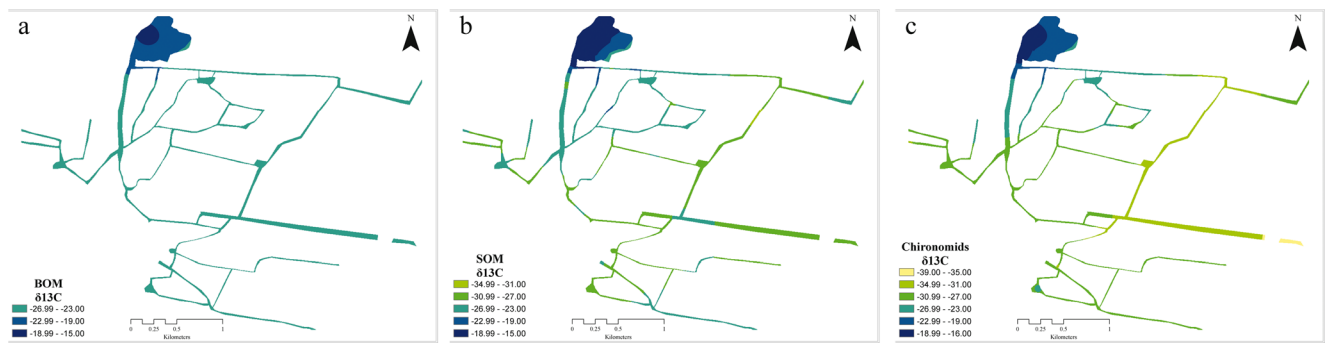
$\delta^{13}\text{C}$  signatures in the BOM, SOM and chironomids showed a similar pattern among the zones (Fig. 2a). Most of the zones had values between  $-30\text{‰}$  and  $-25\text{‰}$ ; the only zone with values close to  $-18\text{‰}$  was XEP.  $\delta^{13}\text{C}$  values differed significantly among the zones for each of the three variables: BOM ( $H=23.17$ ,  $p<0.01$ ); SOM ( $H=45.39$ ,  $p<0.01$ ) and chironomids ( $H=18.31$ ,  $p<0.01$ ; Fig. 2a). Additionally,  $\delta^{15}\text{N}$  values differed significantly among the zones for BOM ( $H=19.0$ ,  $p<0.01$ ) SOM ( $H=45.38$ ,  $p<0.01$ ) and chironomids ( $H=45.32$ ,  $p<0.01$ ; Fig. 2b).

Interpolations showed similar patterns for the  $\delta^{13}\text{C}$  values of BOM (Fig. 3a), SOM (Fig. 3b) and chironomids (Fig. 3c). A homogeneous pattern in this isotope signature was observed



**Fig. 2** K-W ANOVA differences in isotopic signatures among zones. **a.**  $\delta^{13}\text{C}$ ; **b.**  $\delta^{15}\text{N}$





**Fig. 3** Interpolation map using  $\delta^{13}\text{C}$  values: **a.** BOM, **b.** SOM and **c.** Chironomid

along most of the canals. Conversely, there was a heterogeneous pattern for  $\delta^{15}\text{N}$  within and among the canals for the three sampled variables. The canals in the east central and northeastern areas had higher values than the canals in the southwestern area (Fig. 4).

## Discussion

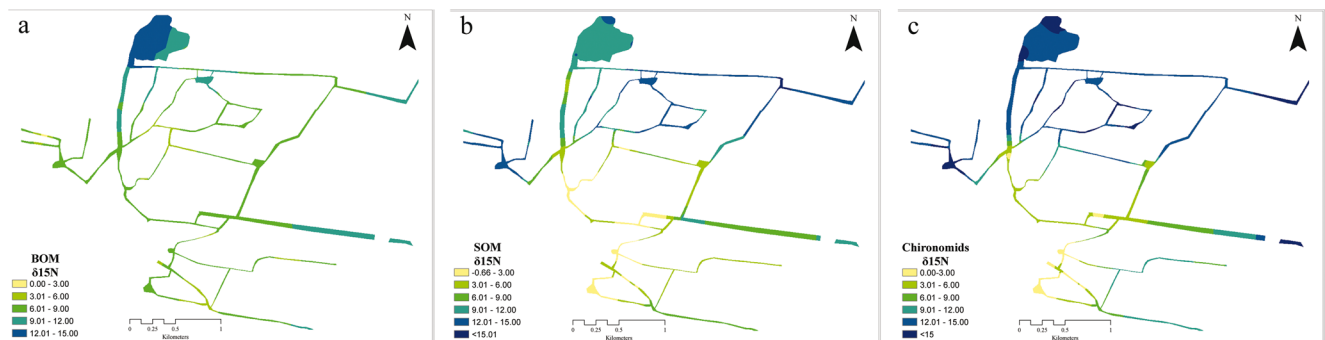
The results suggest that land use in Xochimilco has a differential influence over isotopic nitrogen signatures. However, this influence appears to be less clear for carbon signatures, because the values did not significantly vary along the system. This homogenous carbon isotopic signature can be explained by the similar water source (treatment plants; Legorreta 2009), which appears to have a higher influence than the land use. Also, thin layer of sediments in XEP compared to the rest of the system (personal observation) may have an influence on the signatures. An opposite result was found for the nitrogen isotope values, which were highly heterogeneous, even within the same canal.

Based on the  $\delta^{15}\text{N}$  values for SOM and chironomids, we can split Xochimilco into two regions: the southern region, where Urban and Touristic Zones are located; and the northern region, with primarily agricultural land uses. Although the Agricultural Zone receives water from the Touristic and Urban Zones, the regionalization is clearly defined based on physicochemical parameters (Zambrano et al. 2009), suggesting that the spatial relationship between zones is less important.

Nevertheless, an influence of the Urban Zone over the Agricultural Zone cannot be completely discarded.

Dead organisms usually form an important component of detritus (Moore et al. 2004). Therefore, differences on food webs structure and community composition might be reflected in local isotopic signatures of BOM and SOM (Gu 2009; Kendall et al. 2001). However, all the community structure differences among the zones in Xochimilco have also been related to land use (Contreras Ruiz Esparza 2012; Merlo 2014).

An alternative explanation is related to anthropogenic activities in different land uses in each zone, because  $\delta^{15}\text{N}$  enrichment is commonly associated with human anthropogenic disturbance (Chang et al. 2002; Lefebvre et al. 2007; Peterson et al. 2007). Nitrogen isotopes profiles have also been strongly related to the eutrophic status of lakes (Gu 2009). The effects of these dynamics on the northern and southern regions of Xochimilco appear to differ. The southern region (Touristic and Urban Zones) is considered as hypereutrophic (López-López et al. 2010) and shows low average  $\delta^{15}\text{N}$  values with high spatial heterogeneity. Values of  $\delta^{15}\text{N}$  near zero are found in agricultural systems in which artificial chemicals are used (Nakano et al. 2003) or with a high presence of nitrifying cyanobacteria (France and Schlaepfer 2000). These characteristics appear to occur in the southern region, with a higher proportion of greenhouses than the rest of Xochimilco (Merlín-Urbe et al. 2012). This region also has a greater number of fecal coliforms compared with the Agricultural Zone (Zambrano et al. 2009), with a



**Fig. 4** Interpolation map using  $\delta^{15}\text{N}$  values: **a.** BOM, **b.** SOM and **c.** Chironomid

variety of fecal bacteria such as *Escherichia coli*, *Klebsiella* sp. and *Enterobacter* sp. (Mazari-Hiriart et al. 2008). These coliforms are capable of fixing nitrogen under anaerobic conditions (Jones and Bradshaw 1996; Gauthier et al. 2000), which could be reflected in the nitrogen isotopic signature.

Although the northern region receives water from Urban and Tourist Zones, this region presents nitrogen isotopic signature values that are significantly higher than the south. The northern region, which is eutrophic (López-López et al. 2010), shows relatively homogeneously high nitrogen isotopic values throughout the canals, which belong to Agricultural, Mixed and XEP Zones. These high isotopic signatures have been reported in organic material from urban waste water (Leavitt et al. 2006) and organic fertilizer (Kellman and Hillaire-Marcel 2003). The northern part of Xochimilco is mainly composed of the traditional Agricultural Zone in which artificial fertilizers are not used (Zambrano et al. 2009).

The BOM values were more homogeneous than the chironomid and SOM signatures for both isotopes. This result suggests that the dynamics differ between sediments and the water column. SOM and BOM are both composed of different trophic groups, and therefore their isotopic signatures are based on a mixture of organisms. However, at higher resuspension levels, these microbiota mix (Jonge and van den Bergs 1987; Wainright 1987; Dupuy et al. 2013), and might show similar isotopic signatures. But the lack of a correlation between SOM and BOM signatures suggests a low resuspension of sediments in the water column (Peterson 1987; Hodell and Schelske 1998; Fortino et al. 2009). This is surprising considering the high abundance of carp and tilapia in the system (Zambrano, et al. 2010b), the local motorboat traffic (Garrad and Hey 1987) and the activity of traditional boats (*trajineras*), which are propelled by a pole that is inserted into the sediment. These factors do not appear to produce a substantial re-suspension of sediment in the water column. In addition, wind effects normally cause the re-suspension of sediment (Bloesch 1995; Bailey and Hamilton 1997), but in this case, the small fetch of the system and the trees growing along most of the canals may reduce wave action on the water surface.

The high proportion of SOM contribution to the chironomid mixture suggests that the primarily source of matter for chironomids is not based on sediments. Indeed, the low contribution of BOM to chironomids, added to the apparent absence of chironomids at the bottom strata (possibly by anoxic conditions) of the system, suggests a reduced or even a broken influence of benthic energy. The loss of benthic pathways has been described when a system becomes hypertrophic, most likely as consequence of a switch in primary production (Vadeboncoeur et al. 2003), thereby reducing the prevalence of specialized sediment species (Tewfik et al. 2005).

The isotopic signatures describe a regionalization of the Xochimilco wetland produced by different influences. This is similar to the zonification of Xochimilco based on chemicals in the water (Zambrano et al. 2009). For example, water in the Agricultural Zone is more turbid than the other zones, whereas the Urban and Touristic Zones have the highest values of nutrient concentrations (Zambrano et al. 2009).

The isotope signatures of Xochimilco show that there is an influence of land use on urban wetlands. This influence is different for each isotope signature. An understanding of the different influences over isotope signatures is important for a better management and restoration system for Xochimilco. With this, it is possible to identify and control specific pollution sources affecting each zone, which is critical for this urban wetland that provides of essential ecosystem services to Mexico City (Aguilar Ibarra et al. 2013) and is the last remaining distribution area of the microendemic axolotl (*Ambystoma mexicanum*; Contreras et al. 2009).

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