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CONTENTS

ENVIRONMENTAL PLANNING AND MANAGEMENT OF CITIES AND REGIONS – EDITORIAL

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Cities and regions are highly complex systems in terms of spatial organization and function, as well as in terms of governance, management and policy. They are subject to major urban and economic developments, as well as more recent challenges such as climate change, crises in terms of energy, food and funding, and increasing environmental vulnerability. Appropriate planning and management not only has to accommodate future urban growth but also guarantee environmental sustainability.

This Special Feature in the first part of this issue of the European Journal of Environmental Sciences on Environmental Planning and Management for cities and regions contains six papers on the following issues: urban sustainability policies, urban mobility plans, environmental effects of traffic management strategies, environmental pollution due to road traffic, water saving in tourist units and green tourism supply chain management.

The first paper introduces and depicts a way of setting and managing policy priorities in urban planning. Urban planning addresses the needs and capacities of a city using a multidisciplinary scientific and political process, which regulates urban development taking into account other components of the urban environment. Decision support tools are essential for developing urban strategies for cities, which involves all those who live, work, invest and use all the facilities in a city, as well as visitors and many others.

One of the most important components of an urban environment is transport. Three contributions on this special feature address transportation and sustainable mobility.

Appropriate planning of transport could increase the degree of its sustainability for societies and local authorities. Traditional planning of urban transport reacts to the increasing demand for improved mobility by constantly increasing the infrastructure; whereas sustainable urban mobility planning provides a more holistic approach that aims to maximize the efficiency of the transport system and minimize environmental degradation. Land Use and Transport Interaction models should be integrated into all phases of the Sustainable Urban Mobility Planning process and used to analyze, synthesize and test alternative mobility plans as part of the sustainable spatial planning process and decision making.

Moreover, it is important to evaluate the environmental effects of traffic management schemes and pedestrianization in an urban area. Traffic congestion in urban areas results in increased energy consumption and vehicle emissions. Although pedestrianization aims to promote awareness of the historic environment of cities, it results in an increase in fuel consumption and emissions. Sustainable transport systems limit polluting emissions, waste, etc. and attempt to ensure that the planet's ability to absorb these pollutants is not exceeded. Traffic management plans that not only alleviate traffic congestion but also mitigate the environmental effects of vehicular traffic are necessary.

In terms of global fuel combustion and the related CO_2 emissions the transport sector accounts for an estimated 23%, of which almost three-quarters is attributed to road traffic. Although the road traffic sector is the main emitting source in urban areas, there is a growing concern about the consequences of wildfires in peri-urban forests. It is of utmost importance to investigate and integrate into environmental models the effects of forest fires on carbon emissions, air pollution, biodiversity and climate change dynamics. There is an interesting contribution in this special issue on a joint analysis of the pollutants produced by road transport in a city and the reduction of the carbon sequestration capacity of regional forests around the city before and after wild fires.

The last two papers are on the tourism sector, which is considered one of the most dynamic and far-reaching economic sectors in the world. Apart from a key driver for socio-economic progress, tourism can be responsible for the environmental deterioration of tourist areas, as tourist activities often exert great pressure on natural and anthropogenic environments. Both papers focus on the accommodation sector. Hotels cause significant environmental stress in both natural and urban environments due to their high consumption of water and energy. In addition, the production of large volumes of liquid and solid wastes have a very significant effect on the environment. The aim of the first paper is to assess the environmental performance of mid-sized hotel units by analyzing and quantifying their use of water in order to develop a means of achieving a sustainable consumption. The last paper presents a robust methodological approach for developing Green Tourism Supply Chain Management

(GTSCM) in the hospitality sector, based on estimates of the environmental effect that can be attributed to each link in the supply chain. It is proposed that Life Cycle Analysis (LCA) and Life Cycle Thinking (LCT) should form the basis for efficiently promoting GTSCM in the tourism industry. If the proposed methodology is used properly and consciously by the hotel industry, it will not only help hotel companies improve their efficiency and reduce costs but also contribute to the greening of TSCM at tourist destinations.

INVOLVING DECISION-MAKERS IN THE TRANSFORMATION OF RESULTS INTO URBAN SUSTAINABILITY POLICIES

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ABSTRACT

Mind mapping tools are used to stimulate thinking about sustainability and define its significance for urban planning. Such tools are based on keywords that are identified and structured through dialogue-based procedures. The approach can be used also for switching between highlighting sectorial aspects, such as territorial management and urban design, social and economic cohesion and cross-sectorial aspects, such as sustainable mobility and energy efficiency. This paper emphasizes a structured dialogue with desicion-makers at national, regional and local levels, aimed at identifying what decision-makers really need to decide and the key barriers to the implementation of existing urban sustainability tools. This study was organized in four discrete steps. Initially, what EU urban sustainability projects can deliver (studies, methodologies, tools, policies, etc.) was identified. The deliverables were evaluated against certain criteria and categorized into cross-cutting aspects (territorial management and urban design, social and economic cohesion) and sectorial aspects (sustainable mobility, energy efficiency). The structured dialogue was implemented in parallel with the evaluation of the deliverables in order to match them with decision-makers' needs, priorities and expectations. The ultimate goal was to develop and make available an operational Decision Support System (DSS) for public Authorities and urban planners, which combines their needs, priorities and expectations (structured dialogue results) with existing deliverables, developed within the framework of EU projects that up to now have had a low transferability and applicability rate.

Keywords: Urban sustainability policies, decision-making, structured dialogue, decision support system

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Introduction

There are two features of a classic Mediterranean city that make it more suitable as a human habitat, while being conducive to a lower consumption of natural resources; compactness and complexity. The compactness of a city means that the buildings are grouped closely together, creating a dense environment and a sufficient critical mass of people that there is a high level of different activities, and therefore a transfer of information and relationships. Complexity goes hand in hand with compactness and reflects the diversity of human activities that are located in different parts of the city.

The idea of sustainability in urban models involves the interplay of territorial actions on the city configuration combined with environmental and landscaping elements and the optimal management of natural resources, while promoting social cohesion and the participation of citizens (Perry and May 2010; Perry 2013). It is not possible to work on a part of an urban mosaic, without taking into account its effect on other elements, thus holistic urban planning is a crucial process.

Urban planning is a multidisciplinary scientific and political process for regulating urban development taking into account other components of the urban environment (transport, green spaces, etc.). On this basis, urban planning addresses the real needs and capacities of a city. Planning enables stakeholders to visualize alternative future scenarios that are more sustainable, economically productive and responsive to trends and challenges, and facilitate decision-making and mobilization and empowerment of communities. Urban planning can also promote more efficient, eco-friendly cities through the densification of urban settlements and of mixed land-use, the integration of infrastructure, housing services and the careful shaping of public spaces as well as natural urban areas (Hodson and Marvin 2010).

Decision support tools are essential for producing an urban development strategy for a city, which is mapped out for all those who live, work, invest and interact with all kinds of activities in the city, as well as for visitors and many others. Dialogue-based methods (structured dialogue) for decision-making by politicians and citizens on the formulation of an urban sustainability strategy clearly take preference in this process.

Methodology

A structured dialogue is a process implemented with decisions-makers in order to identify sustainable urban policies and the barriers encountered in implementing European urban policies and their national adaptations. It aims to identify what decision-makers really need and the key barriers to the implementation of sustainable urban policies in the EU (Reed et al. 2006).

This process was used by a research team at the Aristotle University in Thessaloniki, in an effort to help decision-makers adopt existing tools, methodologies and policies within the framework of EU projects and key European initiatives that can be effectively and easily used to meet their needs and priorities in the field of urban sustainability. A mechanism (methodology) was developed and followed in order to support the transferability and applicability of deliverables by the decision-makers.

Based on this methodology, three decision-makers, related to the same kind of sustainable urban policy, were selected by the research team. This avoids getting lost in many different policies and enabled the decision makers to focus on one specific aspect (either sectorial or cross-sectorial). The sectorial aspects were: territorial management and urban design, social and economic cohesion. The cross-sectorial aspects were sustainable mobility and energy efficiency. The specific sectorial aspects where selected for two reasons: (i) They are aspects of vital importance for the transformation of results into urban sustainability policies in Mediterranean cities and (ii) They are top priorities in the scientific and political process for regulating urban development in the study area: Thessaloniki, Greece.

Criteria for Selecting the Decision-Makers

Decision-makers were very carefully selected based on the following criteria:

(i) Responsibility and influence: Decision-makers should be politicians (elected representatives, who can draft policies) or high-level public administrators (people in charge of urban projects, like new areas and developments, who can implement the policies sector by sector). According to the methodology, both politicians and high-level administrators should be selected.

(ii) Field of competence: Two options were offered, as follows:
   - As the interviewer might be interested specifically in some deliverable projects, decision-makers with knowledge of these topics could be chosen.
   - Interviewers could also choose decision-makers that are not experts in those topics, but knowledgeable about current trends in urban sustainability policies.

(iii) Decision-making level: All levels (national, regional, local) should be represented.

(iv) Political diversity: As sustainable urban policies depend also on ideological points of view, the political parties present in the European Parliament should also be represented.

Holding of Interviews with Decision-Makers

The structured dialogue was based on a Questionnaire containing both closed and open-ended questions. The main fields of the Questionnaire dealt with the following issues:

(i) Policies for urban sustainability in general: the most important urban problems in the political or technical agenda were discussed. The following policy areas were ranked: energy efficiency in buildings, sustainable transport, sustainable urban planning, lighting, waste, economic development, architectural heritage, according to the decision maker's view.

(ii) Application of European legislation on urban sustainability: Problems that hinder the implementation of European legislation affecting urban sustainability aspects were discussed.

(iii) Barriers about sustainable urban policies, among:
   - Internal barriers in the administration such as technical/lack of competence, financial barriers, regulatory and legislative barriers, lack of governance tools, lack of partnership and organisational instruments to support the involvement of different social actors, wrong policies with respect to urban problems.
   - Political barriers, such as opposition of some representatives and lack of political support, change of political agenda, conflicts between the priorities of the different decision-makers.
   - External barriers, such as acceptability by citizens and the beneficiaries of the actions and the different priorities of the people involved, economic crises that can change expectations of people, weak instruments and methods to involve citizens.

(iv) Needs and expectations about policies for urban sustainability: In this section, which is crucial for decision support, priority is given to issues that decision-makers wish to improve or focus on, in order to enhance the policies they wish to implement. In addition, the needs of decision-makers for developing urban sustainability policies, e.g. in selecting different typologies of instruments, such as incentives, direct actions, taxes, rules, voluntary instruments, personnel, competences, innovative instruments, funds, etc., were discussed. Availability of finance or tools with long-term effects or to resolve immediate urban problems and/or emergencies were exposed. Existing European activities and initiatives addressing the constraints and needs previously expressed were discussed as well as suggestions for the next program to support some priorities and policies for 2014–2020.

Decision Support Tool

The results of the structured dialogue are the main input for the Decision Support Tool used to support the transferability-capitalization of outputs of former EU projects to the decision-makers. An operational platform, the main feature of the tool, was developed and used. The platform is an operational instrument/interface that has the ability to enhance the transferability of current and future results developed within the framework of EU projects, in a comprehensible and practical way and according to decision-makers' needs and priorities, previously recorded during the structured dialogue process.

A series of outputs – deliverables (either studies, or tools, methodologies, etc.) developed within the framework of EU projects that can be transferred and used by other cities aiming to enhance sustainable urban development are selected and categorized in respect to four axes: (i) territorial management and urban design, (ii) social and economic cohesion, (iii) mobility and transport, (iv) energy efficiency. Both the structured dialogue approach and the outputs in the platform of the DSS are determined by the same urban sustainability definition. The deliverables are categorized by type, being policy papers, or operational tools, or best practices or guidelines, approaches, methodological schemes, etc. Then, considering a set of transferability criteria and the realistic needs and priorities as expressed by decision makers at the national, regional and local levels the results are evaluated by a Scientific Committee (experts from different disciplines and nationalities under a transnational common strategy).

Based on the above, the capitalization platform of the DSS includes EU project deliverables, re-organized and reformulated according to decision-makers' priorities, in order to offer solutions or to improve policies able to mitigate their problems.

The research of the team at the Aristotle University of Thessaloniki, can be depicted schematically as in Fig. 1.

Based on the above a structured dialogue was held for the region of Central Macedonia located in the northern part of Greece, between the Aristotle University Thessaloniki's research team and the following representatives:

(i) President of the Organization of Planning and Environmental Protection of Thessaloniki, representing the national level.
(ii) High-level administrator in charge of the permanent committee for spatial and urban planning and development of the Technical Chamber, department of Central Macedonia, representing the regional level.
(iii) Deputy Mayor of the City of Thessaloniki, representing the local level.

The most important common barriers affecting the implementation of sustainable urban policies identified by all three levels of political governance were:

- Non-existence of a strong political vision for the cities.
- Lack of metropolitan governance – flexibility and co-operation between local and regional administrations (lack of administrative integration).
- Non-implementation (or low implementation) of existing tools for metropolitan governance.

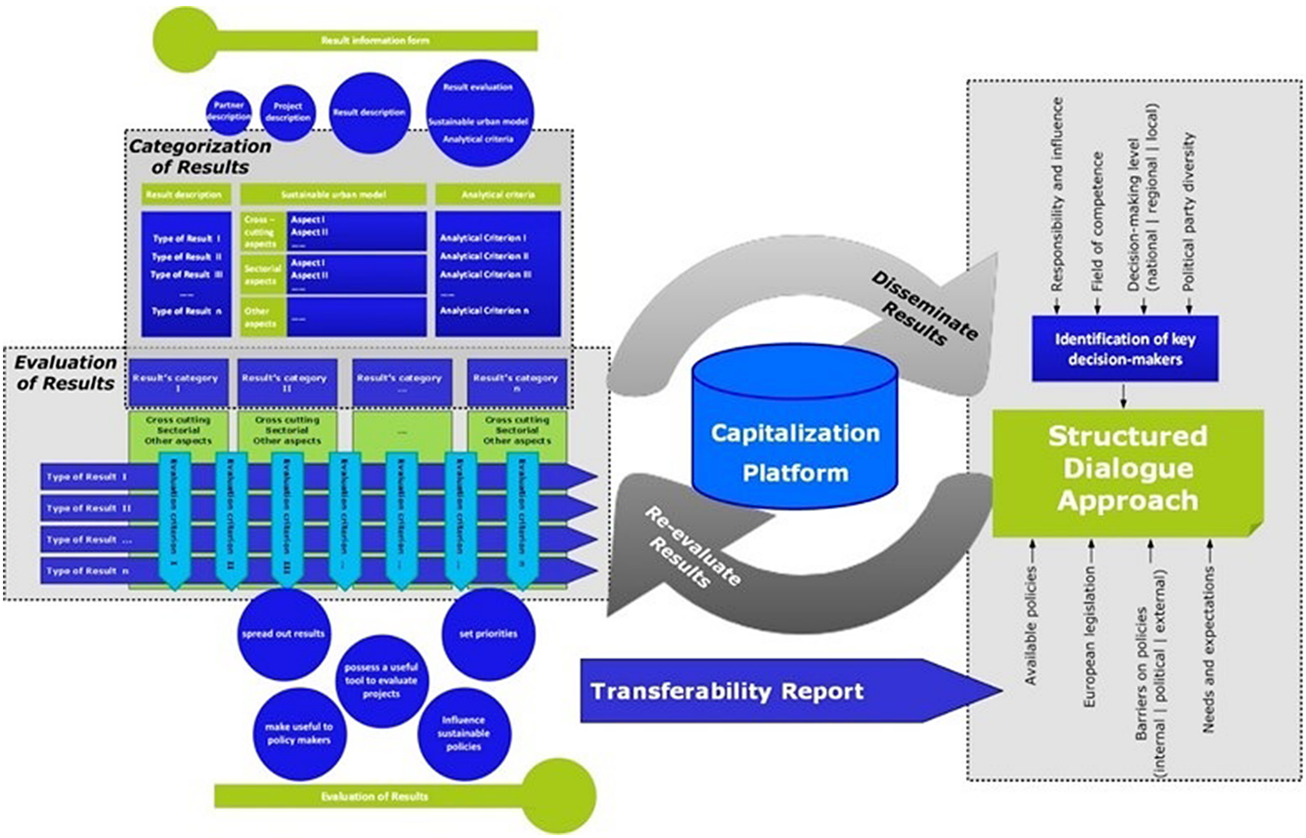

Fig. 1 Schematic approach of the DSS for public Authorities and urban planners.

– Financial issues (low ability to finance urban sustainability projects in cities).
– Conflicts between national regulations (from different Ministries).
– Inability of regional and local administrators to formulate and/or modify the regional, local regulatory framework, and adjust it to the regional and local needs, respectively.
– Opposition of some participants, due to conflicts between priorities of different decision makers.
– Weak methods of involving and mobilizing citizens.
– Lack or wrong policies concerning sustainable development.
– Financial crises that lead cities to deal with different priorities.

The suggestions expressed by the representatives are summarized as follows:
– Enhancement of metropolitan governance and use of existing tools.
– Strengthening of the role of local and regional government, by increasing resources and institutional responsibilities.
– Better collaboration between local and regional authorities and replacement of out of date bodies with more flexible schemes.
– Continuity and consistency in administration, regardless of changes in personal, by means of permanent mechanisms for monitoring the implementation of agreed projects at national or local level.
– Better coordination – the legislative initiatives of different Ministries should not be contradictory.
– Strengthening and establishment of methods for increasing social acceptance of different projects, public consultation, promotion and dissemination of good policies, rewards for effective citizen participation, etc.

All decision-makers agreed that there is great need for enhancement of the metropolitan governance and common decision making based on a clear vision for a city and for better use of the existing financial tools. Collaboration between different economic interests in the exploitation of new funding mechanisms is also of great importance. In terms of financing, the difficulties in optimizing its use, is linked to the poor administrative coordination between Authorities, slow spreading of information, "tight" deadlines, immature proposals and lack of specialized human resources for the timely preparation of proposals. Also, the bureaucratic procedures and the institutional and legal framework affect the ability to utilize the available financial sources.

Conclusions

This paper introduces and depicts a way of setting and managing policy priorities in urban planning. According to the results of the structured dialogue involving decision-makers representing national, regional and local levels in the area of Central Macedonia in Greece, the main findings regarding the national level is the need for the introduction of EU policies that address spatial management in a holistic way. Individual components, such as microclimate, desertification, etc., exist in the regulatory framework, but there is lack of an integrated approach. Also, there is a gap at the national policy level for urban and peri-urban landscapes. At the regional level there is a need to increase mobility and remove obstacles to the transfer of employees and goods, which would enhance the means of transportation within the region of Central Macedonia and the wider buffer zone. Also there is a need for prevention and management of natural disasters (floods, forest fires, earthquakes). Finally, at the local level the improvement of the economic environment and the enhancement of social cohesion are of great importance as well as the promotion of local products and initiatives. The results of the structured dialogue were used to assess the transferability of outputs from EU urban sustainability projects. In this respect, the DSS where the former outputs are categorized and uploaded serves as a platform for public Authorities and urban planners that seek solutions to transform them into urban sustainability policies.

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INTEGRATION OF LUTI MODELS INTO SUSTAINABLE URBAN MOBILITY PLANS (SUMPS)

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ABSTRACT

A literature review indicates that there is an increasing number of Land Use/Transport Interaction (LUTI) models being used in policy analysis and support of urban land use, transport and environmental planning. In this context, LUTI models are considered to be useful for the development of scenarios during the preparatory stage of Sustainable Urban Mobility Plans (SUMPs). A SUMP can be defined as a strategic planning framework, proposed by the European Commission, for planning and design of an urban multimodal transport system, which combines multi-disciplinary policy analysis and decision making. The objective of a SUMP is to achieve sustainable urban mobility, i.e. accessibility for all, safety and security, reduction in emissions and energy consumption, efficient and cost-effective transport and an improvement in the urban environment. Based on the overall conceptual and methodological framework of LUTI models (Geurs and van Wee 2004), the scope of the proposed research is to fully integrate a LUTI model into a contemporary transport planning framework and, more specifically, into the SUMP structure. This paper focuses on the configuration of the integration pattern, according to which a LUTI model may evolve and interact with the planning process throughout the eleven elements of the SUMP, as well as the evaluation of the benefits and drawbacks from the implementation of the proposed pattern for the enhancement of SUMP and overall promotion of sustainable urban planning.

Keywords: land use and transport integrated model, sustainable urban mobility plan, integration, interaction, evaluation

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Introduction

The land use system illustrates the spatial organization of the network of socio-economic activities and describes the physical separation between them. The transportation system connects the various activities/land uses, but at the same time, leads to new mobility and accessibility conditions that may create new time-space relationship between land-uses (Rodrigue 2013). In addition, transport infrastructure consumes a significant part of the available space, especially in urban areas, and may produce fragmentation and segregation effects (Seiler and Folkenson 2006; EEA 2013).

The analysis of the interaction between the two systems: transport and land use is nowadays established as a core issue of mobility planning due to the emergence of the concept of sustainable mobility. In opposition to traditional urban transport planning, where the increasing demand in mobility coped with the constant increase in infrastructure, sustainable urban mobility planning is a more holistic approach that aims at the maximization of the efficiency of the transportation system and minimization of externalities, i.e., environmental degradation.

The investigation of the interaction between transport infrastructure and spatial development is based on two different methods (Pitsiava-Latinopoulou and Zaharaki 2004): (a) the empirical studies 'before' and 'after' the construction of a transport project and (b) the Land Use/Transport Interaction (LUTI) models. A LUTI model is a tool for supporting strategic planning by estimating trends in locational choices and forecasting land use patterns by combining features such as mobility patterns, socio-demographic characteristics, industry allocation, geomorphological and environmental factors, availability of urban networks and institutional and policy frameworks (Pozoukidou 2010). Recently LUTI models have attracted the attention of the scientific community in terms of their role in strategic transport planning, since they are considered to be the most appropriate tool for achieving an understanding of the cause and effect relationship between transport and land use.

At the same time the European Commission (EC) promotes the aforementioned sustainable planning approach for urban mobility within the framework of Sustainable Urban Mobility Plans (SUMPs) (European Commission 2013). A SUMP is a strategic plan that fosters a balanced development of all modes of urban transport, while encouraging a shift towards more sustainable modes, by a combination of inter-disciplinary planning and policy analysis, and decision making. Its objectives coincide with the components of sustainable mobility, i.e., accessibility for all, efficient and affordable mobility services, enhancement of safety and security, decrease of emissions and improvement of energy efficiency and an improvement in the urban environment. More specifically, it covers the whole planning process from the preparatory and goal setting stages to the elaboration and implementation stages through a series of elements that correspond to the specific objectives of the plan, each comprising a set of activities. The plan unravels in a circular pattern and concludes by setting the basis for the implementation of the next SUMP (Bührmann et al. 2013).

The SUMP guidelines recommend a combination of appropriate techniques, such as quality management and benchmarking, with efficient tools, such as indicators and models, for the successful implementation of the activities and fulfilment of the objectives. For this it is suggested that the use of a LUTI model during the preparatory stage of the SUMP could provide an analysis of the effect of the transportation system on locational choices (Bührmann et al. 2013). Based on this suggestion, the objective of the current paper is to investigate the possibility of integrating a LUTI model into the SUMP cycle.

Integration of a LUTI Model into a SUMP

A Brief Description of Sustainable Urban Mobility Plans

The European Commission promoted the Sustainable Urban Mobility Plan (SUMP) as the common framework for the strategic planning for sustainable mobility in European cities (European Commission 2013). In this context, the implementation of SUMP is promoted through policy documentation, programmes, initiatives and financial support instruments related to the objectives of sustainable transportation and urban development. The main feature of a SUMP is the integration of:

- The decision-making mechanism by embedding the main European strategies for sustainable mobility (European Commission 2009) and ensuring the involvement and commitment of national and local authorities, stakeholders and society through the allocation of responsibilities and public consultation.
- Successful inter-disciplinary planning approaches, such as the Plans de Deplacements Urbains implemented in France and the Local Transport Plans implemented in the United Kingdom.
- Planning and evaluation tools, such as monitoring indicators, forecasting models, SWOT (Strengths-Weaknesses-Opportunities-Threats) analysis, etc.
- Priorities and measures for all transport modes in terms of balanced competition and co-modality.

The goals of sustainable development are central to setting the priorities of a SUMP. In particular, a SUMP should be able to describe a long-term and comprehensive set of priorities and related measures for the: a) Social inclusion in the provision of efficient and affordable transport services, b) Improvement of the safety and security of transport activities, c) Enhancement of the quality of the urban and natural environment, the decrease of the transport system's carbon footprint and management of natural resources and energy and d) Economic development and strengthening of competitiveness.

A SUMP unravels in a circular way the whole process of strategic planning, i.e. the identification of the general scope, the formulation of specific goals and targets, the analysis and forecasting of mobility features, the definition and implementation of measures and the monitoring and evaluation of effects. In this way, the plan ends with an update and review of the implementation results and identification of the key-features that will lead to the implementation of another SUMP cycle. According to the guidelines (Bührmann et al. 2011), the aforementioned cycle includes the following 4 phases and 11 corresponding steps:

A. Preparation
   1. Investigation of potentials
      1.1 Commit to overall sustainable mobility plans
      1.2 Assessment of effect of regional/national framework
      1.3 Conduct self-assessment
      1.4 Review of availability of resources
      1.5 Definition of a basic timeline
      1.6 Identification of key actors and stakeholders
   2. Definition of the development process and scope of the plan
      2.1 Look beyond your own boundaries and responsibilities
      2.2 Strive for policy coordination and an integrated planning approach
      2.3 Planning of stakeholder and citizen involvement
      2.4 Agreement on a work plan and management arrangements
   3. Analysis of the mobility conditions and development of scenarios
      3.1 Preparation of an analysis of problems and opportunities
      3.2 Development of scenarios

B. Goal setting
   4. Development of a vision for sustainable urban mobility
      4.1 Development of a common vision of mobility and beyond
      4.2 Actively inform the public
   5. Setting of priorities and measurable targets
      5.1 Identification of the priorities for mobility
      5.2 Development of smart targets
   6. Definition of measures
      6.1 Identification of the most effective measures
      6.2 Learning from others' experience
      6.3 Consideration of the best value for money
      6.4 Use synergies and create integrated packages of measures

C. Elaboration
   7. Allocation of responsibilities and resources
      7.1 Assignment of responsibilities and resources
      7.2 Preparation of an action and budget plan
   8. Formulation of the monitoring and assessment process
      8.1 Monitoring and evaluation process
   9. Adoption of the SUMP
      9.1 Check the quality of the plan
      9.2 Adoption of the plan

9.3 Create ownership of the plan (official adoption of the plan with the involvement of citizens and stakeholders)

D. Implementation

10. Management and communication

10.1 Management of the implementation of the plan

10.2 Information and engagement of citizens

10.3 Check progress towards achieving the objectives

11. Overall evaluation

11.1 Update the current plan regularly

11.2 Review the achievements – understand success and failure

11.3 Identification of new challenges for generating the next SUMP

Each step comprises a set of activities that are essential for achieving the milestones of the corresponding phase, i.e. the conclusion of the analysis of problems and opportunities, the identification of measures, the adoption of the plan and conclusion of the assessment of the final effect.

Land Use Transport Interaction Models

Land use/Transport interaction models (LUTI) are the way planners use the capabilities of personal computers to process quickly, reliably and accurately large volumes of spatial data. The first generation of LUTI models were developed in North America in 1950s, where rapid economic growth and the need for systematic study of the interactions between land use and the transport system set the conditions for the creation and exploitation of the first urban models (Brail and Klosterman 2001). Since then the use of LUTI models, is in many cases, a prerequisite to long-term and medium-term strategic plans for sustainable urban development. International literature refers in great detail to the use and utility of LUTI models, as tools for evaluating the effect of urban development policies (U.S. EPA 2000; Spiekermann and Wegener 2004). Actually it was the passage of two federal policies in USA in the early 1990s (Clean Air Act and Intermodal Surface Transportation Act) that introduced the LUTI models used by academics into the planning practice.

LUTI are spatial interaction models used in urban models of a planning process, the first generation of which were static synthetic economic and spatial interaction models. The theoretical background of these models is based on regional economics, locational theories and urban economics. Therefore they embody the principle of land suitability, as a result of the interaction between economic production factors. In particular, it was Von Thunen in 1826 that set the basis for locational theories by making the simple assumption that production of goods at a certain site will continue only if the profit from this activity (profit minus production cost) is greater than the cost of the transport of goods. Much later in 1964, Alonso incorporated in this theory the principle of land suitability and land bid rent curves for household and business, while Sinclair in 1967 used the theory of Von Thunen to explain the phenomenon of urban sprawl.

From a mathematical point of view choice of location is determined by exponential or logarithmic models based on the method of utility maximization and entropy or random utility by setting limitations to the cost of transport determined, in most cases, by income. These mathematical models calculate the probability of occurrence / establishment of a particular type of land use or urban function taking into account all of the factors mentioned above (transport, rent, etc.). They incorpo-

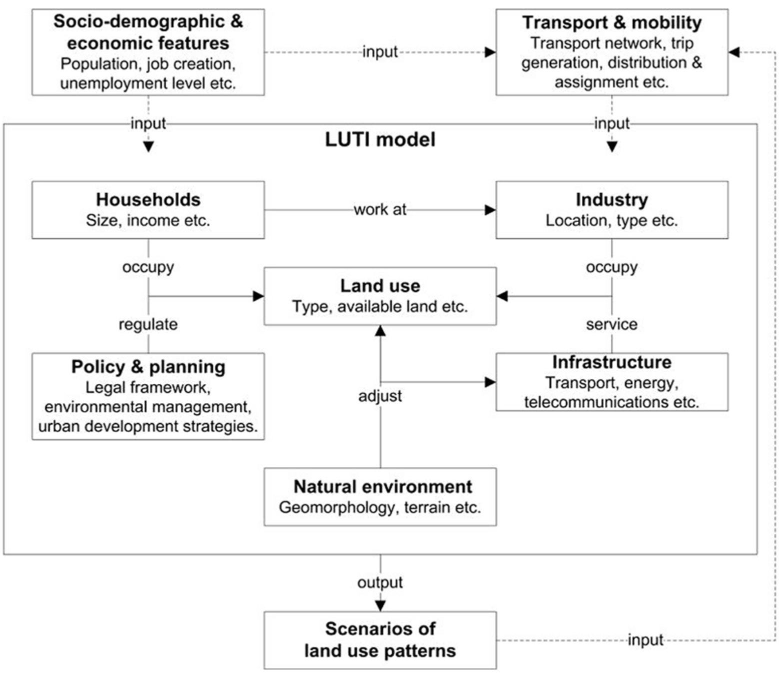

Fig. 1 Structure of a typical LUTI model.

rate a four stage transportation modeling process i.e. trip generation, trip distribution, modal split and modal assignment and therefore are very suitable for an integrated land use transport approach.

More specifically LUTI models can be used to support strategic planning by estimating trends in locational choices and forecasting land use patterns by combining the features of mobility, socio-demographic characteristics, industry, geomorphology and wider environmental factors, and the availability of urban networks and institutional and policy frameworks (Pozoukidou 2010). According to Fig. 1, the available infrastructure and physical characteristics of the wider urban space and the way these features are taken into account by the planning and policy framework create the conditions that determine where industry is located. These choices affect the locations of households that work in the industry depending on their demographic and socio-economic features and the demands placed on the transport system. In this way, the model is able to produce forecasts of future land use patterns. Thus LUTI models can contribute to strategic transport planning and significally improve the efficiency of the planning process.

Based on this concept various LUTI models with different approaches were developed during the late 1970s and 1980s. Examples are those of Lowry, Putman, Echenique, Anas, Wegener and others (Putman 1992; Wegener 2004; Johnston et al. 2006). However, many of the early models were criticized for being very costly to implement due to the high requirements for collecting and managing data relative to their ability to produce valid and case-specific results. Since then, the development of computers and new technologies that are able produce and manage geo-spatial data through Geographic Information Systems (GIS) and emergence of concepts like sustainability, resilience and holistic planning, are nowadays leading to the enhancement of existing and development of new operational LUTI models.

Description of the LUTI Model Integration Framework

The proposed framework for the integration of a LUTI model into the SUMP cycle is based on maximising the potential contribution of an integrated land use/transport model for the successful conduction of the aforementioned activities is presented in Fig. 2. There are four (4) phases and eleven (11) Actions that formulate the proposed LUTI integration framework corresponding to the four (4) phases and the appropriate activities of the eleven (11) SUMP steps. More specifically, either the outcome of an Activity of the SUMP cycle (from here on referred to as SUMP Activity) can be used as the input for the corresponding action for the integration of the LUTI model (from here on referred to as LUTI Action) or a LUTI Action can provide outputs for the support of a SUMP Activity, as described in the following sub-sections.

Phase 1-Predictive (Strategy oriented): The first phase of the proposed integration framework aims at the selection and preparation (adjustment) of the appropriate LUTI model and the development of the strategic scenarios. The results from the deployment of strategic scenarios are expected to support the analysis of problems and opportunities, according to the SUMP's first Milestone.

The first LUTI Action is the definition of the model's scope in relation to the needs of the specific study. This action depends on the following SUMP Activities:

1.1 – determining which sustainable mobility principles will be adopted by the plan and how;
1.2 – which involves among others the analysis of the transport and land use policy priorities that need to be taken into account by the model;
1.6 – aims at defining the network of stakeholders from the different transport related sectors.

The next LUTI Action refers to the selection of the most suitable model and its adjustment to the plan's purpose. This depends on the aforementioned scope and on SUMP Activity 1.5, i.e. the setting of the plan's timeline, which will define the dynamic characteristics of the model and the time scale of the short and long-term forecasts.

After the selection of the most suitable LUTI model, the formulation of strategy based scenarios, i.e. a series of scenarios based on the strategic approach of the plan are developed as suggested in SUMP Activity 3.2 (Bührmann et al. 2011). However, in order to formulate resilient and realistic scenarios, one should take into consideration the analysis of problems and opportunities, conducted during SUMP Activity 3.1.

The final action of this phase is the assessment of the strategy based scenarios, which are expected to lead to generic forecasts of urban development patterns according to the urban mobility strategies examined. These forecasts can be exploited in the context of SUMP Activities 4.1 and 5.1, which aim, respectively, to identify the strategic directions and setting of specific priorities for sustainable urban mobility planning. Moreover, the demonstrative capabilities of the model can create a space for discussion among stakeholders and public (SUMP Activity 4.2).

Phase 2-Predictive (Target oriented): During the second phase, the LUTI model can be updated according to the quantified targets set by the second stage of the SUMP in order to provide more detailed forecasts of the possible effects of the selected measures' for the enhancement of urban mobility on the land use system. In this way the model can contribute to the SUMP's second milestone, i.e. the identification of suitable measures.

Specifically, SUMP Activity 5.2 results in the development a series of Specific, Measurable, Achievable, Real-

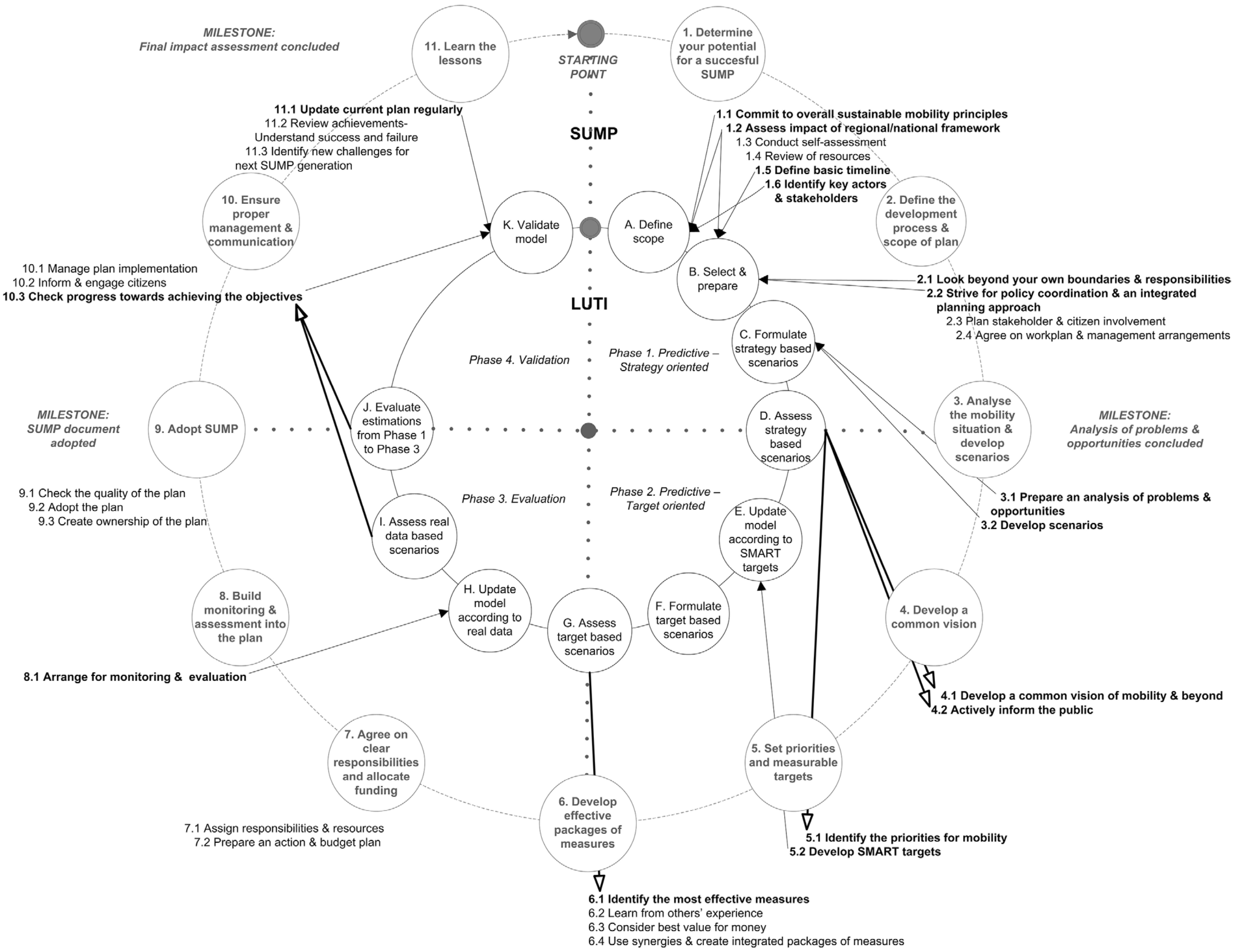

Fig. 2 Framework of the integration of a typical LUTI model into a SUMP cycle.

istic and Time-bound (SMART) targets by selecting and formulating a set of indicators. The corresponding LUTI Action aims at updating the model according to these targets so it is able to produce estimates of indicator values (especially the ones related to the effect of transport on land use) in different time projections. After the formulation of scenarios based on the appropriate combinations of transport related measures and interventions, the target based model can be used to estimate the effect of these measures on the land use system and support the decision making of SUMP Activity 6.1 in identifying the most effective measures.

Phase 3-Evaluation: In this phase the LUTI model is updated based on real data derived from the regular monitoring of indicators during the elaboration of the SUMP and the provision of accurate estimates that can be used to check the progress during the implementation of the SUMP at the milestone in the adoption of the plan.

SUMP Activity 8.1 refers to regular monitoring of a core set of measurable indicators for the evaluation of the plan's elaboration. These measurements can be used as input in the LUTI Action for updating the model. Then, the updated model can be used to reassess the target based scenarios using real data and reach conclusions on the progress of the implementation of the plan and the achievement of its objectives in terms of the goals related to urban development. Furthermore, the review of the assessment of the use of the model in the strategic, target and real data based scenarios should be made in order to evaluate progress in terms of achieving the objectives of the integrated urban and transport plan.

Phase 4-Validation: The objective of this phase is the overall validation of the contribution of the LUTI model to the SUMP's last milestone, i.e. the assessment of the final effect, and the necessary changes and adjustments for its implementation in the next SUMP. Towards this end, the results and conclusions of the following SUMP Activities,

10.3 – Check progress towards achieving the objectives,

11.1 – Update current plan regularly,

should be embedded in the LUTI Action for the model's validation. This process will ensure that the model is kept up to date with the whole SUMP cycle and is suitable for future use.

Applications of the Proposed Integration Framework

It is quite obvious that integration of LUTI models into SUMPS could bring substantial benefits to contemporary strategic planning. Nevertheless application of the proposed framework for the full integration of such models into a SUMP cycle may be limited by several operational bottlenecks.

The most frequent barriers faced during the preparation and implementation of a SUMP is the lack of necessary expertise, absence of political support, limited funds and an inadequate legislative framework. Significant difficulties can also be encountered during the public participation process, a key element in a SUMP. These difficulties mainly concern the limited funding for organizing such processes, the low level of interest and awareness on the part of citizens and stakeholders, the limited tradition in organizing and participating in such processes and the inability of vulnerable groups to express their opinion when up against more influential groups.

Moreover, metropolitan urban areas are in need of a more integrated and comprehensive approach to transport planning. The issues that are related to the transport of persons and goods cannot be addressed by each municipality separately, but requires the existence of a transport authority at the metropolitan level. European legislation provides the framework for the establishment of public transport authorities with broad responsibilities, which include planning, operation and management of multi-modal and alternative transport systems. The advantage of these authorities, which are established in cities like London and Bologna, is that they are staffed with highly qualified multidisciplinary personnel. In contrast, in cities lacking such authorities, overlapping responsibilities and allocation of tasks occur, when at the same time there is lack of appropriate scientific capacity that is particularly needed in the case of the integration of a LUTI model in a SUMP.

The issues associated with the application land use models might be due to reasons that are related to the functionality of the LUTI model per se. These problems are mostly related to the data needed in order for the LUTI models to run the emended calibration and validation processes. The quality of results of these processes are critical for the operation and outcomes of the model and are very dependent on data quality and availability (Pozoukidou 2014). Other concerns about appropriate data are compatibility issues, as the data for LUTI models must be consistent (spatially and temporally) with data used for transport models within a SUMP cycle (Pozoukidou et al. 2015). In addition, there are several usability issues associated with LUTI models, which are extensively discussed in the literature (Vonk et al. 2005). Most of the studies conclude that although these models are commonly used by academics, they are rarely used in policy making and planning. This is due to the fact that these models are conceptually and operationally complex and potential users do not have the technical skills or knowledge to use such models (Pozoukidou 2008). To overcome this problem there have been several efforts to develop more user friendly LUTI models that take into account the requirements of policy makers, which can be integrated into the collaborative decision making process.

Conclusions

This paper demonstrates how LUTI models could be integrated into all four phases of the SUMP process, for the analysis, synthesis and testing of alternative mobility plans. It also demonstrates that integration of a LUTI model into the SUMP cycle is a very efficient means of achieving the strategic goals of the SUMP. Therefore, full integration of LUTI models into a SUMP cycle enhances its strategic and communicative aspects, mainly because LUTI models can be used as testing and evaluating tools, and for communicating and ensuring mutual understanding amongst the stakeholders. Finally, the importance of such integration is related to the fact that assessing the effects of alternative mobility plans on choice of locations, has been recently the core concern of the much desired and theoretically discussed interdisciplinary approach in sustainable transport planning. Nevertheless the success of the proposed approach depends on several operational and institutional aspects that still need to be addressed.

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ROAD TRANSPORT CARBON EMISSIONS AND FOREST SEQUESTRATION CAPACITY IN THE REGION OF ATHENS BEFORE AND AFTER FOREST FIRES

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ABSTRACT

One important component of the urban contribution to carbon dioxide atmospheric emissions is road transport. Carbon dioxide (CO_2) emissions from urban road transport in the centre of Athens recorded over a period of five years (2000–2005) are compared with the carbon sequestration capacity of regional forests, prior to and after the devastating forest fires in Attica in 2007 and 2009, which is the administrative region of Athens. The comparison of carbon flow reveals two complementary aspects of the same socio-environmental issue: persistent sources versus weakening sinks for CO_2 within a mixed (urban and rural) setting. Road transport emissions are calculated bottom-up using traffic data from in-situ measurements along segments of main roads. The sequestration capacity of forests is estimated by combining satellite images of changes in land cover with literature values of biomass growth rates. Over the study period, the per capita CO_2 emissions averaged 0.72 t CO_2/cap/year, which is four times higher than the sequestration capacity of forests before and six times higher after the fires. This imbalance highlights the inadequacy of the local carbon sink. Although there is no biogeochemical need to neutralise carbon budgets locally, defining the CO_2 flows from urban activities and local ecosystems is likely to raise awareness and promote global environmental sustainability. The results are compared with top-down estimates of CO_2 emissions at a regional scale, where suburban areas are dominant, and the differences are discussed in the light of local socioeconomic factors.

Keywords: road transport, peri-urban forests, fires, carbon emissions, carbon sequestration, Athens

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Introduction

Human driven alterations in the global carbon (C) cycle mainly result from the combustion of fossil fuels and deforestation, both of which add carbon dioxide (CO_2) to the atmosphere and oceans. Atmospheric concentration of CO_2 is currently 30% above pre-industrial levels (Steffen et al. 2007) as a result of a long term global disequilibrium between carbon emission and sequestration rates. Growing forests and oceans are the main CO_2 sinks. Oceanic storage is governed by physicochemical processes and biological feedback mechanisms with different responses to increasing levels of atmospheric CO_2 (Samiento et al. 2004; Fung et al. 2005; Schuster and Watson 2007), which many argue is likely to weaken the future capacity of the oceanic sink and, therefore, accelerate climate change (Sabine et al. 2004; Schuster and Watson 2007; McKinley et al. 2011). In contrast, forest biomass allows permanent storage of CO_2. However, forest growth depends on competition for land with human land uses, such as agriculture, housing and transport infrastructure, which are land intensive activities and often respond to land scarcity by expanding into adjacent forests (Lambin et al. 2001; FAO 2009; Napton et al. 2010). Conversion of forests into built-up land and wild forest fires are common examples of land use changes with net releases of CO_2 (Roy 2003).

In particular, forest fires are a major environmental issue in Greece (Hadjibiros 2001) and many other Mediterranean countries characterized by long periods of dry and hot weather conditions (Papakosta et al. 2014). Pine forests and shrubs, especially at low-altitudes in peri-urban areas (Wildland Urban Interface), are among the most threatened types of vegetation (Chas-Amil et al. 2013; Papakosta et al. 2013). The issue of climate change raises further concerns about a possible increase in the frequency of wildfires (Giannakopoulos et al. 2011).

Typically in the literature, the issue of the capacity of forests to sequester carbon and its reduction due to forest fires are addressed separately from the issue of anthropogenic emissions of specific economic sectors. On the one hand, there is an increasing knowledge of energy consumption and of trends in the emissions from road transport and their possible effects on human health and global climate (He et al. 2005; Chapman 2007; Piecyk and McKinnon 2010). The contribution of transport to global fuel combustion and CO_2 emissions is estimated at 23%. Road traffic is responsible for almost three-quarters of these emissions (IEA 2014; Grote et al. 2016). On the other hand, global scale environmental effects of forest fires, including emissions of carbon, air pollution, biodiversity and climate change dynamics are increasingly being investigated and integrated into environmental modelling (Amiro et al. 2001; Randerson et al. 2006). However, the quantitative relations between forest fires and CO_2 emissions at the local scale are rarely studied. This study is such a joint analysis of road transport in Athens, the capital of Greece, and the reduction in the carbon sequestration capacity of regional forests around Athens before and after wild fires. This comparison combines two aspects of the same socio-environmental issue: changes in the emissions from a specific sector of urban activity in suburban areas under human pressure. Although carbon sources and sinks are not necessarily balanced locally, comparisons that put specific urban activities and ecosystem changes into a common perspective are likely to promote awareness of city dwellers of local and global environmental issues.

This is a bottom-up study of the CO_2 emissions, which generates data at scales that are not covered by more macro-scale methods that rely on average and aggregated information. We provide in the discussion a comparison of the results obtained at the local scale with the emissions reported in top-down studies and relate the differences to socioeconomic factors influencing mobility.

This paper is organized as follows. Section 2 describes the methods for estimating road CO_2 emissions and the sequestration capacity of regional forests. Section 3 presents the results and provides a quantitative ratio for the emission and absorption rates. Section 4 focuses on differences between bottom-up and top-down studies of road CO_2 emissions and discusses possible explanatory socio-economic factors and the local environmental effects of fires. Finally, a short conclusion summarizes the findings of the paper.

Methods and Data

Road Transportation and CO_2 Emissions

We consider the direct and indirect emissions of CO_2 (Chi and Stone 2005) from road transport within the area of the Athens prefecture and Piraeus. The population in this continuous urban area makes up more than 25% of the population in Greece. The average population density in this area is 7,638 inhab/km².

Direct emissions are those from the combustion of fuel by the road transport system, which depends on the distances travelled, fleet composition, fuel use per vehicle category and fuel emission factors. Indirect emissions are those associated with the construction and maintenance of roads, manufacturing, servicing and scrapping of vehicles (Jonsson 2007) and drilling for, refining and distribution of fuels (Lane 2006). Indirect emissions may be accounted for in terms of the percentage of the direct emissions. This paper calculates direct emissions for the period 2000–2005 based on *in situ* measurements of traffic volumes (Zamba 2006; Zamba and Hadjibiros 2007). Indirect CO_2 emissions associated with the construction and maintenance of the roads are assumed to be equal to 40% of the direct emissions (Jonsson 2007).

Traffic data was collected for 16 main roads (Fig. 1, red lines) on which the traffic is typical of that of Athens. These roads are in the so-called ‘greater ring’ of Athens, which is the center of the social and cultural activities of the Greek capital (Fig. 1, black lines). The annual distances travelled, fuel consumption and CO_2 emissions calculated for this area are extrapolated to all roads in the greater ring of Athens based on geometrical data derived from road maps.

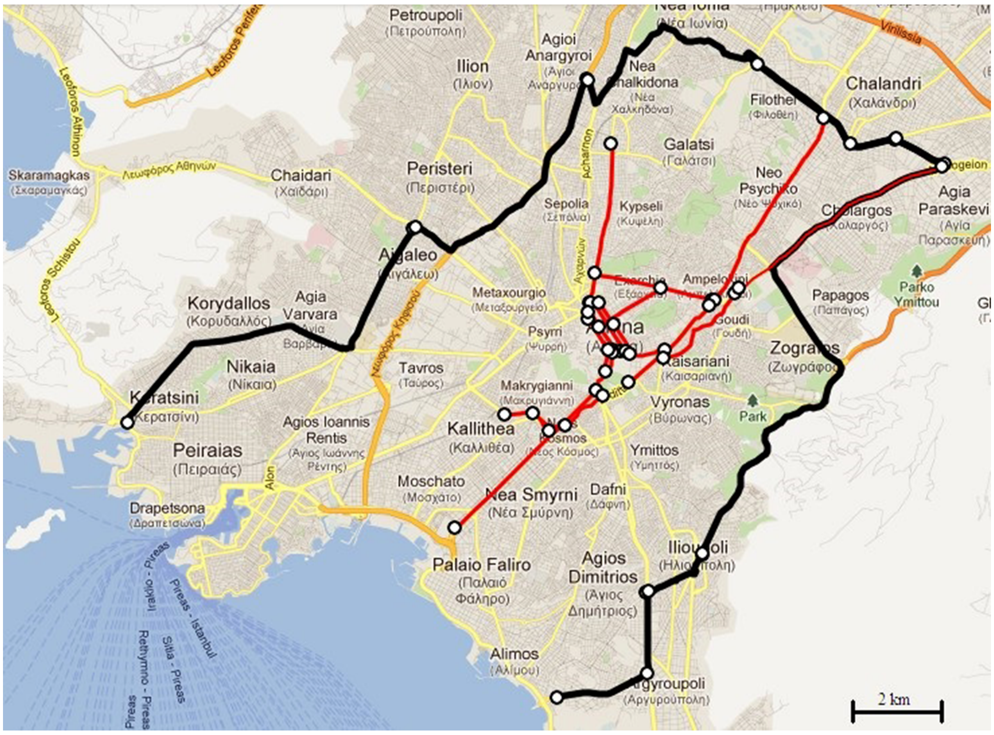

Fig. 1 The "greater ring" (black perimeter) in Athens and the 16 main roads (red lines) for which data on road traffic was collected. Source: Google Maps.

Estimates of the Carbon Sink

The carbon sequestration capacity of growing forests depends on the area of forest and biomass growth rate. The area classified as forest covers about 43% of the area in Attica. Changes in the sequestration capacity of the forests on Mounts Parnitha, Aigaleo, Penteli, Hymettus and the North-East mountains (Fig. 2) were determined before and after the big fires of 2007 and 2009. The dominant tree species in these ecosystems were broadleaved (shrubland) and coniferous trees such as Aleppo pines and firs. The growth rate of these species largely determines the sequestration capacity of the entire ecosystem. Therefore, a simple way to assess whether the carbon stock of the whole ecosystem is increasing or decreasing is to compare the frequency with which trees are destroyed to the typical growth timespan of the main species. Forests before reaching the climax stage are typically carbon sinks. The growing periods of Aleppo pines and firs are several decades while the frequency of major fire events in the region varied from a few years to about two decades over the last century (Hadjibiros 2001). As an example, since 1913, 438 fires have been recorded on Mount Parnitha. These fires destroyed the entire forest at least once, and, specific parts of it up to six times (Amorgianiotis 2007; Karani 2008). Similarly, according to the Greek Ministry of Agriculture, the coniferous forest on Mount Penteli was decimated by three big fires between 1995 and 2000, while Mount Hymettus experienced 59 important fires from 1980 to 1993 and several smaller fires later. The fire history of the North-East Mountains in Attica is similar, though there are no precise records. This evidence support the hypothesis that the forest ecosystems around Athens were mostly far from climax and therefore absorptive in both 2007 and 2009.

The areas of forest before the fires were derived from geographical data using the Google Earth application (http://earth.google.com/download-earth-advanced.html) and two other free-access geographic information system applications (GE-Path freeware, version 1.4.4 (http://www.sgrillo.net/googleearth/gepath1_4_4_exec.zip and GEO-UTILITIES online tools, http://geo-news.net/index_geof.html). Areas of interest were enclosed by polygons and measured in terms of land area. The measured vegetation included trees, shrubs and other evergreen sclerophyllous plants. However, there is no detailed inventory of the vegetation covering these areas. Burnt forest area was determined from satellite images using Keyhole Markup Language files (.kmz) from relevant websites. Data on burnt forests are taken from Latsoudis (2007), Tilaphos (2008) and EFFIS (2009). Data from EFFIS include type of vegetation, whereas other data sources only provide aggregate data.

The carbon sequestration capacity was calculated using a uniform sequestration rate and equation (1) (IPCC 2006):

$$C = A \times G_w \times (1 + R) \times CF \qquad (1)$$

where C is the annual increase in biomass of carbon due to forest growth (tons C/year), A the area of land covered by growing forest (ha), G_w the average annual above-ground biomass growth rate (tons DM/ha/year), R the ratio of below-ground biomass to above-ground biomass (tons DM below-ground biomass/tons DM above-ground biomass) and CF the fraction of carbon in total dry matter (tons C/tons DM). To express carbon sequestration in terms of carbon dioxide, the predictions of equation 1 are multiplied by 44/12 (the weight ratio between carbon dioxide and the carbon atom). Values for G_w, R and CF (respectively; 4.0, 0.4 and 0.5) are taken from IPCC (2003), Mokany et al. (2006) and Lamlom and Savidge (2006) for vegetation in Greece.

Results

Total distance travelled, energy use, direct and indirect CO_2 emissions and the corresponding areas of forest for carbon sequestration (the energy footprint) in hectares from 2000 to 2005 are detailed in Chatzimpiros et al. (2015) based on data from Zamba and Hadjibiros (2007). The weighted average fuel consumption of vehicles is 0.09 l/km and corresponding CO_2 emissions 219 g CO_2/km; the annual per capita CO_2 emissions average 0.72 t CO_2/cap/year and the total required sequestration area is about 200 × 10^3 ha. Table 1 shows

Table 1 Distances travelled, energy use, carbon emissions and the carbon sequestration requirements of road transport in Athens.

Year	Total annual distance travelled by vehicles (10^9 km)	Energy used for vehicle propulsion (PJ)	Direct CO_2 emissions (Mt)	Indirect CO_2 emissions (Mt)	Total CO_2 emissions (Mt)	Total area of forest (kha) required for sequestration
2000	7.3	23.0	1.4	0.6	2.0	198.0
2001	7.3	23.0	1.4	0.6	2.0	197.9
2002	7.3	23.0	1.4	0.6	2.0	198.0
2003	7.1	23.0	1.4	0.6	2.0	194.7
2004	7.2	22.9	1.4	0.6	2.0	197.1
2005	7.1	22.5	1.4	0.6	2.0	194.2
Average	**7.2**	**22.8**	**1.4**	**0.6**	**2.0**	**196.7**

total distance travelled, energy use, direct and indirect CO_2 emissions and the corresponding area for carbon sequestration in hectares.

The fires of 2007 and 2009 destroyed almost 40% of the forest biomass in the Attica region (Table 2). Fig. 2 gives an overview of the burnt sites (red colour) and of the remaining standing forest (green colour). Significant parts of the burnt area were 'Natura 2000' zones or belonged to the National Park of Parnitha. Comparing carbon emissions and sequestration revealed that the sequestration capacity of forests was about four times lower than the road CO_2 emissions before and about six times after the fires. There was, therefore, a significant imbalance and decrease over time because of the fires, in the CO_2 sequestration capacity of the regional forests compared to the road CO_2 emissions.

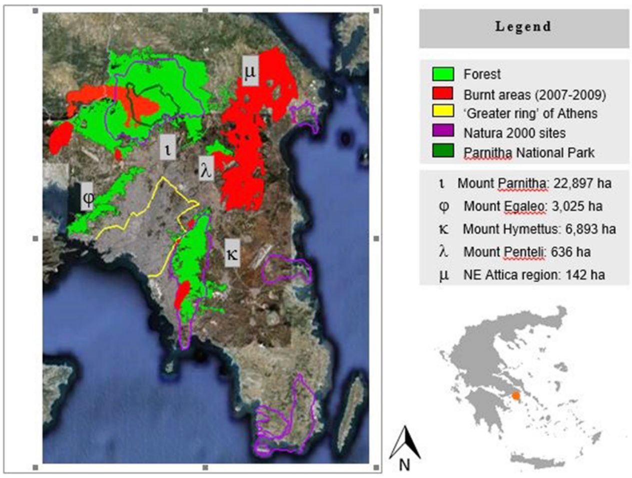

Fig. 2 Burnt (red) and remaining forest (green) in the Attica region after the 2007 and 2009 fires.

Table 2 Changes in carbon sequestration (kt/yr) by forests around Athens between 2006 and 2009.

Forest area (ha)		Annual C absorption (kt/yr)	Annual CO_2 absorption (t/yr)
Burnt	19.094	−53	−196
Remaining	33.593	94	345
Total	52.687	148	541

Reduction in absorption is denoted by "−".

Discussion

The sequestration of CO_2 resulting from fuel combustion by vehicles and the construction and maintenance of the road system in the prefecture of Athens and adjacent city of Piraeus, which together host 2.9 million people and cover an area of over 370 km², requires an area of growing forest of about 12 times bigger than the urban area itself. Given that 8 hectares of urban area contain about 1 hectare of road network (Zamba 2006), the sequestration of the emissions from 1 hectare of road requires about 100 hectares of forest. During this study, total annual distances travelled remained practically unchanged at around 7.2×10^9 km. This reflects the traffic saturation conditions in the center of Athens, which is a common problem in densely populated cities surrounded by large suburbs with little public transport. However, since 2009, which is the year of the start of the Greek financial crisis, traffic volumes have decreased due to a slow-down in the Greek economy. Accordingly, the calculated emission to sequestration ratio has probably also slightly decreased since 2009. This is an interesting example of an improvement in traffic conditions, with subsequent decrease in environmental degradation without the application of specific road traffic control strategies (Papageorgiou et al. 2003).

The comparison at the local scale of CO_2 emissions from a specific sector with the sequestration potential of forests (and its possible reduction due to fire or changes in land use) is barely addressed in the literature, although the challenge for environmental protection and climate action largely rely on local awareness and behaviour. Such comparisons require bottom-up approaches based on inventories of local data that may deviate from more macro-scale estimates. Deviations can be attributed to heterogeneity and specificities of distinct spatial zones (Wang et al. 2009). The results of this paper are put into perspective in terms of top-down estimates of emissions at national and regional scales. The comparison reveals sub-regional discrepancies in road traffic and emissions. At the national scale in Greece, road CO_2 emissions are estimated at 15.7 Mt in 2000 and 18.22 Mt in 2005 (OECD/IDF 2010). Of these emissions, about 46%, 7.2 Mt in 2000 and 8.4 Mt in 2005, are allocated to Attica. If we downscale this figure proportionally in terms of the population in the study area, the share of Athens and Piraeus in Attica's emissions would be 5.5 Mt in 2000 (~1.9 t/cap/year) and 6.3 Mt in 2005 (~2.5 t/cap/year), which is almost 3 times higher than the emissions calculated in this study (~0.72 t/cap/year). This difference could be partly related to the effects of local driving patterns (series of accelerations, decelerations and frequent stops) on fuel consumption (Tzirakis et al. 2006). Moreover, there are major infrastructural and socioeconomic differences between Athens and its administrative region that imply that a simple population-based downscaling of emissions would be problematic. The differences in emissions in relation to socioeconomic factors influencing mobility are discussed below.

The population density in the whole Attica region is about 990 cap/km². If Athens and Piraeus are excluded, the figure drops to 270 cap/km², against 7 638 cap/km² in the study area. This 30-fold difference is very significant with respect to road CO_2 emissions because fuel consumption decreases exponentially with urban density (Newman and Kenworthy 1999). In addition, the public transport network in Athens is much denser than in the rest of Attica. As a consequence, the dependency on private cars for leisure, home-to-work rides and household food and materials supply is much higher in Attica than in the city of Athens and Piraeus. Moreover, assuming that the attractiveness of the city of Athens generates mobility in the broader Attica region, this mobility is almost exclusively sustained by the use of private cars.

Two additional socioeconomic factors are likely to explain the observed difference. The first is everyday long-distance car driving by Athenian workers to surrounding industrial and tertiary sector zones. The second is frequent family weekend trips to middle-distance country-houses. In both cases, the corresponding emissions mainly result from Athenians living within the study area but mostly driving outside it. The "suburban" share of their trips therefore contributes to the emissions for Attica, which are not included in our measurements.

The corresponding "off-zone" emissions can be estimated by focusing on the main drivers. One main driver is home-to-work-trips, which are quite significant. Almost half of the industrial activity of Greece is located in Attica (ROPA 2007) and in particular in zones that are distant from Athens: in the North, the industrial zones of Kryoneri and Oinofita respectively are about 25 and 55 km from the Northern edge of Athens, in the West are Thriasio and Elefsina with petrol refineries and shipyards at 15 km, and in the East, the plain of Mesogeia, with significant manufacturing activity at 25 km. Many of the employees at these sites are Athenians whose combined daily trips amount to thousands of kilometres.

Regarding weekend trips, hundreds of thousands of Athenian families own secondary residences in the countryside, mainly along the north, east and south coastlines of Attica but also in Evvoia (the big peninsula in the North of Attica) and on the northern Peloponnese. In order to reach these sites from Athens, half of Attica must be crossed. It can be roughly estimated that, prior to the economic crisis, one third of the population of Athens, about 300 000 families, owned countryside houses and made such trips twice per month. This amounts to about 7.5 million family trips per year. Given Attica's geography, average travel distance per family per weekend exceeds 150 km, resulting in annual CO_2 emissions of about 300 Mt, which is 20% of the emissions calculated for the study area. The above assumptions are certainly rough, but reflect the order of magnitude of regional road emissions generated by Athenians. They also provide insights into the factors that need to be accounted for in order to downscale road emissions in heterogeneous areas.

Although there is no detailed information, it is probable that because of the increase in unemployment, long-distance car driving by Athenian workers to surrounding industrial and tertiary sector zones significantly declined after the 2009 crisis. In addition, the frequency of family weekend trips also probably decreased after 2009; such changes may be considered as "positive" consequences of the economic crisis in reducing CO_2 emissions, although the recent decrease in the price of fuel may act in the opposite direction.

The list of the ecological effects of fires extends far beyond the global consequences in relation to greenhouse gas emissions. Major local consequences include the weakening capacity of suburban ecosystems to provide ecosystem services to the local population, such as flood control, regulation of local climate, prevention of soil erosion, recreation activities, etc. They also include effects on biodiversity. The mountains around Athens are rich in plant and animal species. Especially Mount Parnitha, where the effects on biodiversity are significant and possibly irreversible. In 1961 Mount Parnitha became a National Park because it hosted a great variety of flora and fauna including endemic or endangered plants, birds, reptiles, insects, amphibians and mammals (Amorgianiotis and Aplada 2007; Latsoudis 2007). A well-known protected species is the red deer of which the population on Mount Parnitha is the largest and one of the last in Greece. According to post-fire *in-situ* estimates, more than 10% of the deer perished in the fire and a further decline in abundance is expected as about two thirds of the summer biotope of the deer was destroyed (Latsoudis 2007). Mount Parnitha was also rich in species of birds and plants. A total of 132 species of birds are recorded of which about 90 are protected and 6 are rare (Amorgianiotis 1997; Karani 2008). The recovery of these species is doubtful even if the forest fully regenerates (WWF 2009). Concerning plant diversity on Mount Parnitha, 1100 species of plant are recorded for the area destroyed by fire, out of which 92 are endemic to Greece and two (*Campanula celsii parnesia* and *Silene oligantha parnesia*) are endemic to Mount Parnitha (Sfikas 1985; Aplada et al. 2007). Long-term effects on biodiversity are, however, particularly difficult to assess as they partly depend on protecting soil against erosion and grazing, and on a succession of years after the fires when the temperature and humidity conditions are favourable for ecosystem regeneration. The fate of some endangered species also depends on the recovery of other species on which they depend for food and shelter. Fire guard controls and National Parks are means of conserving and protecting natural capital. Since they failed to protect the forests, additional protective measures are needed, especially in the context of climate change, which increases the risk of forest fires occurring (Giannakopoulos et al. 2011). The identification and mapping of the remaining natural areas in terms of biodiversity, land cover and indigenous species is important as it can help raise awareness of individuals of climate change and biodiversity issues and provide basic information needed to implement measures for protecting or reinstating the ecosystem. The inventories must be regularly updated in order to monitor changes in vegetation and plant diversity, identify causes and carry out relevant actions. The absence of basic knowledge may be a major threat to natural ecosystems, since it results in poor or no protection measures.

Conclusions

The comparison of road traffic CO_2 emissions with the sequestration capacity of regional forests in Attica reveals that even before the fires in 2007 and 2009, emissions were greater than the regional carbon sinks. The latter were reduced about 40% by the fires, which highlights an increasing inadequacy of the local carbon sequestration capacity. Protection measures are required to deal with local causes that generate global environmental issues. This analysis also provides an estimate of road CO_2 emissions at an urban scale, for which previously there was no official data. This brings regional official statistics into line with more local measurements and connects the deviations to specific socioeconomic factors. We also conclude that the lack of specific inventories and identification of the remaining ecosystems in terms of ecological value may contribute to their further destruction, because of poor or no protection measures.

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THE USE OF A TRANSPORT SIMULATION MODEL (AIMSUN) TO DETERMINE THE ENVIRONMENTAL EFFECTS OF PEDESTRIANIZATION AND TRAFFIC MANAGEMENT IN THE CENTER OF THESSALONIKI

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ABSTRACT

Traffic congestion in urban areas results in increased energy consumption and vehicle emissions. Traffic management that alleviates traffic congestion also mitigates the environmental effects of vehicular traffic. This study uses the transport simulation model AIMSUN to evaluate the environmental effect of a set of traffic management and pedestrianization schemes. The effects of the pedestrianization of specific sections of roads, converting two-way roads into one-way roads for traffic and changing the direction of flow of traffic along one-way roads were simulated for different areas of Thessaloniki's city centre network. The assessment of the environmental effect was done by determining the predicted fuel consumption and emissions of greenhouse gases (GHG) and air pollutants. Fuel consumption and the environmental indicators were quantified directly using the fuel consumption and emissions model in AIMSUN. A typical weekday morning peak period, between 09:00am–10:00am, was simulated and the demand data obtained using a macroscopic traffic assignment model previously developed for the wider area of Thessaloniki. The results presented in this paper are for network-wide simulation statistics (i.e. fuel consumed, carbon dioxide (CO_2), nitrogen oxides (NO_x) and particulate matter (PM)).

Keywords: environment, pedestrianization, traffic management, microscopic simulation, emissions model, AIMSUN

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Introduction

Pedestrianization is defined as the closing of specific segments of roads to traffic, followed by paving the area and installing street furniture and other details (Hall and Hass-Klau 1985). Pedestrianization schemes aim to promote awareness of the historic environment of cities and increase the value of properties located within traffic-free areas (Chiquetto 1997). However, restricting traffic flow in specific parts of a road network can have substantial implications for local and network-wide environmental conditions. Since traffic flow and speed are the main determinants of levels of air pollution, changes in the patterns of traffic flow inevitably induce changes in the patterns of traffic emissions and fuel consumption (Chiquetto 1997).

There is a study using a mesoscopic traffic simulation model to evaluate the effects of pedestrianization in the city of Chester, UK (Chiquetto and Mackett 1995). Simulation outputs from SATURN (i.e. vehicle queues, traffic flow and travel times) have been used to feed environmental predictive models for estimating traffic emissions. Concurrently, there is an assessment of travellers' response to changes imposed on traffic conditions with respect to mode choice. The results indicate that total fuel consumption slightly decreased, and emissions decreased around the pedestrianized area but increased in the network as a whole.

There is another study that evaluate the effects of pedestrianization on traffic and the environment in the cities of Katerini and Rhodes, Greece (Pitsiava-Latinopoulou and Basbas 2000). This study determined the operation of junctions located near to the main area of pedestrianization using the program SIDRA (Signalized Intersection Designs and Research Aid). The results of this analysis indicated that NO_x, HC and CO emissions decreased significantly along with fuel consumption and average delay per vehicle. In addition, a reduction in road accidents was also recorded near the pedestrianized area.

The change in the performance of traffic (e.g. mean network speed, vehicle-km travelled, etc.) and in environmental indicators (e.g. CO_2 emissions, fuel consumption) after the implementation of pedestrianization schemes in urban areas was assessed for all of the traffic and public transport separately using the traffic mesoscopic simulation model SATURN (Taxiltaris et al. 2002). Findings of this analysis indicate an increase in fuel consumption and emissions in the wider area around the pedestrianized zone. It is proposed that traffic demand management schemes and promotion of public transport should complement pedestrianization and counter their potential negative effects.

The environmental effects of pedestrianization of a major arterial street, as part of an architectural proposal for restoring a Square in Thessaloniki, was evaluated using the traffic simulation model SATURN (Economou et al. 2002). The authors propose the implementation of mitigating measures (e.g. rearrangement of specific traffic signals, alterations in the circulation patterns in the streets around the square) to alleviate the adverse environmental effects of pedestrianization on nearby streets. An ex-ante evaluation of an urban regeneration project in Athens, Greece (i.e. pedestrianization of a major artery in a downtown area) was conducted to identify the effects of traffic (Kepaptsoglou et al. 2015). The findings indicate that traffic conditions would deteriorate in the short-run, but a potential reduction in traffic resulting from this project could significantly improve traffic and environmental conditions in downtown Athens.

Several studies have been done to assess traffic and environmental effects of other traffic management schemes such as conversion of a two-way road to one-way road, changing the direction of flow of traffic along a one-way road and traffic calming measures. Traffic calming combines physical changes in road design and speed management in order to improve road safety, especially for users of non-motorized transport sharing the same road (Lockwood 1997). Traffic calming measures eliminate conflicting movements, improve visibility, reduce exposure and sharpen the attention of drivers (Ewing 1999).

Specifically, a study in Montreal, Canada investigated the effects of isolated traffic calming measures both at corridor and network levels (Ghafghazi and Hatzopoulou 2014). This study was based on the development of a simulation model of a dense urban neighbourhood. The results of this study indicate that on average, isolated calming measures increase carbon dioxide (CO_2), carbon monoxide (CO) and nitrogen oxide (NO_x) emissions by 1.5, 0.3 and 1.5%, respectively, across the entire network. Area-wide schemes result in a percentage increase of 3.8% for CO_2, 1.2% for CO and 2.2% for NO_x across the entire network.

The effects of two traffic management measures (i.e. speed limit reduction and coordinated traffic lights) is reported for an area of Antwerp, Belgium (Madireddy et al. 2011). An integrated model was used that combined the traffic simulation model Paramics with the CO_2 and NO_x emission model VERSIT+. This predicted that when speed limits are lowered from 50 to 30 km/h in the residential part of the study area CO_2 and NO_x emissions are reduced to about 25% and, in addition, the implementation of a green wave signal coordination scheme along an urban arterial road a further reduction in the order of 10% could be expected.

The environmental effects of three different traffic management measures (i.e. optimisation of traffic signals, coordination of traffic signals and urban tolling) was determined for Thessaloniki's urban road network using the traffic simulation software SATURN (Papaioannou et al. 2000). This analysis indicates that the combined implementation of these measures yields the best results in terms of environmental benefits compared to the isolated deployment of each of the aforementioned strategies.

This study evaluates the environmental effects of pedestrianization schemes in the city centre of Thessaloniki using microscopic traffic simulation. The road network in the central business district of Thessaloniki was simulated in AIMSUN. Aggregate and disaggregate simulation output statistics were obtained by simulation and are presented in this study.

Materials and Methods

Microscopic Traffic and Emissions Simulation Modelling

Microscopic traffic simulators can imitate the longitudinal and lateral movement of individual vehicles as they occur in real-life. Their ability to dictate these movements is based on a set of sub-models that replicate a driver's car-following, lane changing and gap acceptance behaviour. Thus, the simulators estimate each vehicle's position, speed and acceleration for every simulation step. The trajectories of the vehicles are then used to estimate fuel consumption and emissions using the corresponding models that are integrated in the microscopic traffic simulation model. A microscopic emission model has been integrated in AIMSUN (Panis et al. 2006). This model is based on empirical measurements that relate vehicle emissions with the instantaneous speed and acceleration of the vehicle. The importance of using microscopic emission models for the assessment of the environmental effects of traffic management and control policies has been explicitly stressed, since this is a complex issue that requires detailed analysis of not only their effect on average speed but also on other aspects of vehicle operation such as acceleration and deceleration (Rakha and Kamalanathsharma 2011).

The Study Site – AIMSUN Model

A detailed microscopic simulation model was developed of the central business district area of the city of Thessaloniki. The model development was implemented using the AIMSUN microscopic traffic simulator. The simulated network is comprised of 401 sections and 290 junctions; its total length is 42 km and is depicted in Fig. 1. Among the 290 junctions, 62 are controlled by signals. Forty public transport lines were also simulated along with their corresponding time plans.

Demand was determined by using a macroscopic traffic assignment model developed in VISUM for the wider area of Thessaloniki (Stamos et al. 2013). Field traffic flow data collected from traffic sensors located throughout the road network of Thessaloniki for a one-hour morning peak period (i.e. 09:00–10:00 am) of a typical weekday (i.e. Wednesday 15th October 2014) was input into the macroscopic model, which executed the traffic assignment and produced the necessary demand information for the "loading" of the microscopic

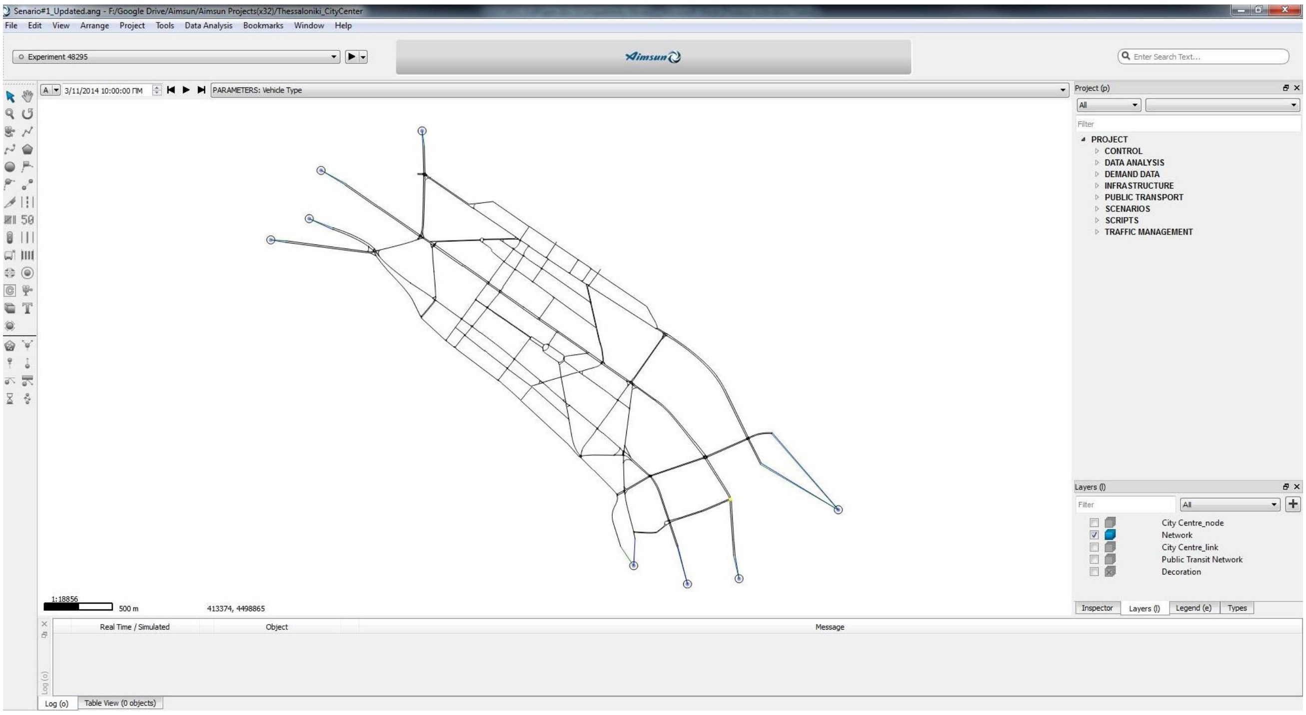

Fig. 1 Simulated network in AIMSUN.

model. Information on traffic composition was also obtained from a previous study (Mitsakis et al. 2013). According to this study the traffic in this portion of Thessaloniki's road network is comprised of 90% cars, 5% taxis, 4% trucks and 1% buses.

The operation and performance of the network was assessed for five different pedestrianization schemes. A total of 6 scenarios were simulated, 1 pertaining to the base case scenario and 5 to the simulated pedestrian areas. The exact measures involved in each pedestrianization scheme are presented in Table 1.

Table 1 Description of scenarios.

Scenarios	Descriptions
Scenario 1	The pedestrianization of A. Sofias St. from Egnatia St. to Nikis Ave., of Keramopoulou St. from P. Ioakim St. to A. Sofias St., of Makenzi King St., of Ermou St. from K. Ntil St. to A. Sofias St., and the conversion of Ermou St. to a two lane one-way street from K. Ntil St. to E. Venizelou St.
Scenario 2	The measures of Scenario 1, plus the conversion of Tsimiski St. to a three lane street, with two general purpose lanes and one bus lane.
Scenario 3	The pedestrianization of A. Sofias St. from Egnatia St. to Nikis Ave., of Keramopoulou St. from P. Ioakim St. to A. Sofias St., of Makenzi King St., of Ermou St. from A. Sofias St. to E. Venizelou St., and the conversion of Ermou St. to a two lane one-way street from K. Ntil St. to E. Venizelou St.
Scenario 4	The measures of Scenario 1, plus the pedestrianization of Nikis Ave. from E. Venizelou St. to E. Aminis St.
Scenario 5	The pedestrianization of Nikis Ave. from E. Venizelou St. to E. Aminis St. and the conversion of Tsimiski St. from a four lane street to a three lane street, with two general purpose lanes and one bus lane.

Due to the stochastic nature of AIMSUN it is necessary to make several runs of each simulated scenario, so that the simulation output is statistically significant. Therefore, five simulations of the base case scenario were initially run, each with a different random seed generated by AIMSUN's internal random number generator, and statistics (i.e. standard deviation and mean value) for the average network speed were determined for this sample of runs. The significance level was selected to be 95%, the tolerable error equal to 0.5 km/h, and given the standard deviation of the average network speed of the initial sample, the required number of runs was determined to be five.

Results and Discussion

The output of the simulations includes traffic performance measures and environmental indicators. Simulation output statistics were estimated both at section level (i.e. disaggregated level) and network level (i.e. aggregated). The estimated traffic performance measures are average section traffic flow and average network speed. The environmental indicators are fuel consumption, CO_2, NO_x, and PM emissions.

Disaggregated Simulation Output Statistics

The local effects of pedestrianization were evaluated for three road sections located close to the pedestrianized areas. The implementation of the pedestrianization schemes resulted in the redistribution of traffic in the nearby road network. It becomes apparent from the simulation results that traffic flow along these road sections increases sig-

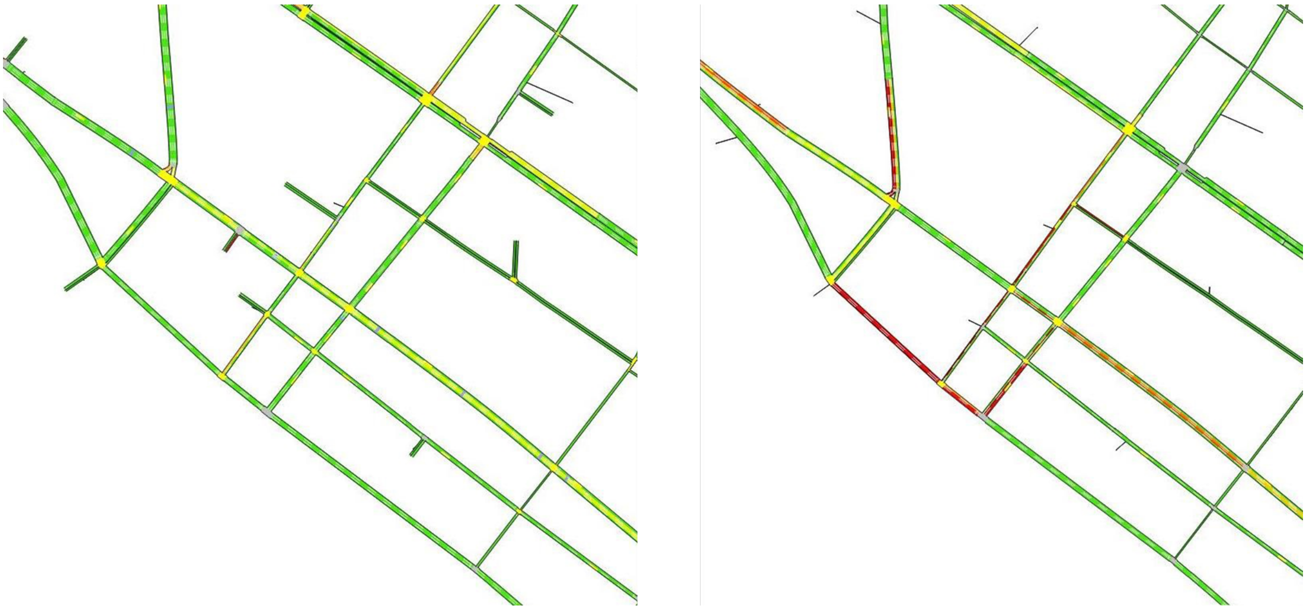

Fig. 2 Pedestranization of Nikis Ave. reduced traffic flow in nearby streets.

nificantly (Table 2) compared to the base case scenario. Consequently, fuel consumption and CO_2 emissions also increase substantially (Table 3 and 4). The increase in traffic density on the nearby road network due to the pedestrianization of Nikis Ave. is explicitly depicted in Fig. 2.

Table 2 Difference in average traffic flow relative to that recorded for the base case scenario (%).

Demand Level	Tsimiski St. (upstream of K. Ntil St.)	Mitropoleos St. (downstream of A. Sofias St.)	E.Venizelou St. (upstream of Ermou St.)
Scenario 1	76.20	11.57	62.14
Scenario 2	72.02	11.10	59.44
Scenario 3	74.05	17.07	77.27
Scenario 4	72.74	74.63	85.53
Scenario 5	64.74	39.93	105.64

Table 3 Difference in average fuel consumption relative to that recorded for the base case scenario (%).

Demand Level	Tsimiski St. (upstream of K. Ntil St.)	Mitropoleos St. (downstream of & A. Sofias St.)	E.Venizelou St. (upstream of Ermou St.)
Scenario 1	45.37	12.91	70.45
Scenario 2	38.02	16.96	70.89
Scenario 3	34.93	25.32	89.52
Scenario 4	41.22	48.71	127.55
Scenario 5	41.49	34.09	112.31

Table 4 Difference in average CO_2 emissions relative to that recorded for the base case scenario (%).

Demand Level	Tsimiski St. (upstream of K. Ntil St.)	Mitropoleos St. (downstream of & A. Sofias St.)	E.Venizelou St. (upstream of Ermou St.)
Scenario 1	60.51	13.34	69.77
Scenario 2	53.25	16.30	70.62
Scenario 3	56.12	24.33	87.78
Scenario 4	56.70	58.41	117.48
Scenario 5	56.38	37.36	117.94

Aggregate Simulation of Output Statistics

The effects of pedestrianization was also assessed network-wide. Since traffic was banned from several road sections, which were converted into pedestrian areas, demand had to be accommodated by the rest of the network. Thus more traffic corresponds to a reduced network capacity and consequently traffic conditions on the whole network deteriorate. The average network speed decreases compared to the base case scenario after the implementation of traffic-free areas (Table 5). Since the average network speed for the base case scenario is 28.23 km/h, it becomes obvious that the average network speed after pedestrianization is less fuel efficient and environmentally friendly. Network-wide traffic emissions rise significantly as a result of pedestrianization (Table 5). The implemented traffic management schemes effect mainly the emission of particulate matter (PM). The magnitude of PM estimated by the model per scenario is presented in Table 6.

Table 5 Difference in average network statistics relative to those recorded for the base case scenario (%).

Demand Level	Speed	CO_2	NO_x	PM
Scenario 1	−10.99	35.54	26.05	76.70
Scenario 2	−12.44	36.54	27.09	79.58
Scenario 3	−10.87	34.35	24.89	73.81
Scenario 4	−18.31	41.08	31.14	86.65
Scenario 5	−20.57	39.64	31.20	80.87

Table 6 Magnitude of PM per scenario estimated using the simulation model.

Demand Level	PM (kg)
Base Case	726.72
Scenario 1	1284.11
Scenario 2	1305.03
Scenario 3	1263.15
Scenario 4	1356.45
Scenario 5	1314.43

Conclusions

The environmental effects of pedestrianization in the city centre of Thessaloniki were evaluated using microscopic traffic simulation modelling. Results indicate that there would be a significant increase in fuel consumption and emissions if pedestrianization is implemented, both locally (i.e. along particular sections of roads) and network-wide. However, no assessment was made of the potential effects of pedestrianization on the demand of the public to travel and their choice of mode of travel that could result in changes in energy consumption and environmental conditions. Moreover, it has to be mentioned that emissions within pedestrianized areas cannot be estimated using microscopic traffic modelling.

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GREEN TOURISM SUPPLY CHAIN MANAGEMENT BASED ON LIFE CYCLE IMPACT ASSESSMENT

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ABSTRACT

Tourism is one of the most dynamic and far-reaching economic sectors in the world. Numerous different and complex activities are involved in the efficient development of tourism. These activities interrelate economic, environmental, social, cultural and political dimensions in the overall supply chain. However, apart from its key role as a driver of socio-economic progress, tourism is responsible for environmental deterioration, not only in areas popular with tourists, but also by enhancing climate change globally. This paper presents a robust method based on the Green Tourism Supply Chain Management (GTSCM) concept, which can be used to estimate the effect on the environment that can be attributed to each link of the supply chain. The overall approach is based on Life Cycle Impact Assessment (LCIA) theory and corresponding models. A case study to demonstrate the applicability of this approach is presented for two large seaside hotels located in Chalkidiki, Greece. Chalkidiki is the most popular tourist destination in Northern Greece. A LCIA questionnaire was developed and input data for the Life Cycle Assessment (LCA) obtained from the hotel managers. For this LCA SimaPro 8 software was used. The LCIA methods chosen were Eco-indicator 99 and CML 2001. The effect on fossil fuel consumption of both hotels due to their use of local transport and electricity was considerable but less than that needed for transporting the tourists by air to Chalkidiki. This paper clearly indicates that LCA and Life Cycle Thinking (LCT) can form the basis for promoting GTSCM in the tourism industry.

Keywords: Green Tourism Supply Chain Management, Life Cycle Assessment, Life Cycle Thinking, Eco-indicator 99, CML2001

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Introduction

Over several decades, tourism has continued to grow and diversify and is currently one of the fastest growing economic sectors in the world (UNWTO 2015). According to the World Tourism Organization, currently the business volume of tourism equals or even surpasses that of oil exports, food products or automobiles. A highly competitive environment has forced tourism companies to adopt approaches already used in other industries such as manufacturing, agriculture, etc. in order to meet the needs of the most demanding customers. One of these is referred to as Tourism Supply Chain Management (TSCM), i.e. supply chain management in tourism-related companies.

According to Zhang et al. (2009), TSCM is defined as a network of tourism organizations engaged in different activities ranging from the supply of different components of tourism products/services, such as accommodation and flights, to the distribution and marketing of the final tourism product at a specific destination, and involves a wide range of participants in both private and public sectors. A typical tourism supply chain (TSC) involves the suppliers of all tourism goods and services that are delivered to the end-consumers (Tapper and Font 2004), as depicted in Fig. 1. The tourism product consists of three principal elements: accommodation, travel and recreational activities (Kuo and Chen 2009) and is perishable (cannot be stored for future use), with the complexity of the TSCM similar to that which manufacturing industry faces in producing and marketing their products (Page 2015; Ling 2015).

Apart from being important in determining socio-economic progress, tourism is responsible for the deterioration of the environment in tourist area (Gössling 2002). In response to the increasing concern of tourists about environmental issues, the tourism industry has switched to “green” in their supply chain (e.g. Budeanu 2009; Odoom 2012). For this reason, the concept of a Green Tourism Supply Chain Management (GTSCM) is promoted in the overall framework of tourism-related activities in order to consider its effect in terms of environmental deterioration and climate change, and initiatives to reduce its effect.

Various definitions of green supply chain management (GSCM) exist in the literature. According to Gilbert (2001), greening the supply chain is the process of incorporating environmental criteria or concerns into organizational purchasing decisions and long-term relationships with suppliers, whereas Zsidisin and Siferd (2001) define GSCM as “the set of SCM policies held, actions taken and relationships formed in response to concerns related to the natural environment with regard to the design, acquisition, production, distribution, use, re-use and disposal of the firm’s goods and services”. Seuring (2004) describes GSCM as the managerial

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integration of material and information flows throughout the supply chain to satisfy the demand of customers for green products and services produced by green processes. Srivastava (2007) defined GSCM as "integrating environmental thinking into supply chain management, including product design, material sourcing and selection, manufacturing processes, delivery of the final products to the consumers, and end-of-life management of the product after its useful life". According to Zhu et al. (2008), GSCM "ranges from green purchasing (GP) to integrated life-cycle management supply chains flowing from supplier, through to manufacturer, customer, and closing the loop with reverse logistics". GSCM covers the following activities: "green procurement", "green design", "green operations and reverse logistics", "green manufacturing" and waste management (Hervani et al. 2005). According to Walker et al. (2008), the green supply chain concept covers all phases of a product's life cycle, from the extraction of raw materials through the design, production and distribution phases, to the use of the product by consumers and its disposal at the end of the product's life.

The present study proposes a robust promotion of GTSCM, based on an estimate of the environmental effect that can be attributed to each link in the TSCM. The overall approach is based on Life Cycle Impact Assessment (LCIA) theory and corresponding models used for operating hotels and transport for tourist. It should be emphasized that hotels belong to the 1st level of suppliers of tourism products (Fig. 1) and are one of the most important agents of a "static" environmental burden in the TSCM (Michailidou et al. 2016). The lodging sector uses vast quantities of energy, water and products. Energy use per guest night can be as much as 98 MJ (Gössling 2002) and water consumption ranges between 84 and 2425 l per guest-night (Gössling 2015). In addition, the lodging industry generates large volumes of waste. A typical guest generates at least 1 kg of solid waste per day (Davies and Cahill 2000), whereas a tourist from developed countries probably generates up to 2 kg per day in the United States (UNEP 2003). According to the literature, amongst other tourism environmental performance tools, Life Cycle Assessment (LCA) is crucial, since it evaluates environmental effects from different perspectives and based on different assumptions (e.g. Filimonau 2016). Furthermore, Life Cycle Thinking (LCT) can result in identifying the processes and/or flows that result in the highest consumption of resources and greatest environmental burden when attempting to estimate the total environmental effect. SimaPro 8 software is used to define the functional units, the boundaries and limitations of the problem under study. LCA and LCT form the basis for efficiently promoting GTSCM in the tourism industry.

This approach is demonstrated for the most popular tourism destination in Northern Greece, Chalkidiki. A comparative "environmental damage" analysis for two large hotels is produced and their respective contribution to the environmental burden is assessed. This approach results in a reliable assessment of damage that can be attributed to accommodating and transporting tourists.

Materials and Methods

TSC (Fig. 1) includes 1st and 2nd level suppliers, tour operators, travel agencies and tourists. 1st level suppliers includes tourism services providers, which directly supply tourism services to tourists or intermediaries (tour operators and travel agents) e.g. accommodation providers (e.g. hotels, camping sites, etc.), transport providers (e.g. renting cars, bus operators, etc.), food suppliers (e.g. restaurants), etc., whereas 2nd level are those who directly supply tourism service providers with products or services, such as energy and water suppliers, food and drink manufactures, waste recycling and disposal services, etc. Travel agents retail tourism products and deal directly with tourists or via tour operators. Travel agents and tour operators can be the same business entities. It should be noted, that the TSC depends mainly on the characteristics of the Defined Area of Concentrated Tourism (DACT), i.e. the tourist destination. Addressing the environmental effect of TSCM at a tourism destination requires an environmental analysis of all of its components/products going back to the raw materials from which they were produced, through suppliers, suppliers' suppliers and so on.

In order to estimate the effects in the TSCM, LCA is carried out in four distinct phases (ISO-14040, ISO-14044), as follows: (i) Goal and scope definition, (ii) Life cycle inventory (LCI), (iii) LCIA and (iv) Interpretation. LCIA attempts to establish linkages between the product or process and its potential environmental effects by addressing ecological and human health effects and resource depletion. The implementation of LCIA requires the LCI, which is an inventory of all input and output environmental flows of a product or service system (Frischknecht et al. 2007).

For LCI, a detailed list of all 1st and 2nd level suppliers, tourism operators and travel agents should be created. For each product or service for every supplier, materials and processes from "cradle-to-grave" should be identified in order to quantify the extraction of resources and emissions of a product system or process to air, water and land and their associated effects (Muthu 2014). This requires questionnaires to be appropriately designed and answered by managers/directors/engineers of each supplier during personal interviews. This is a demanding task, since it entails huge effort and availability of resources.

A number of effect assessment methods for quantifying the environmental performance of a product, process or service are available (JRC 2010). Inventory data is aggregated into specific environmental effect categories according to the selected LCIA. LCIA methods can be single-category (e.g. primary energy) or multi-category, with specific sets of effect categories. Multi-category LCIA methods can be problem-oriented or damage-oriented. An LCIA consists of 4 steps: (i) Classification, where all substances are sorted into classes according to the effect they have on the environment; (ii) Characterization, where all the substances are multiplied by a factor which reflects their relative contribution to the environmental effect; (iii) Normalization, where the quantified effect is compared to a certain reference value (e.g. the average environmental effect of a European citizen in one year); (iv) Weighting, where different value choices are given to effect categories to generate a single score.

Damage-oriented methods, such as the Eco-indicator 99 (Goedkoop and Spriensma 2001), model the cause–effect chain up to the endpoints, namely translate environmental effects into issues of concern such as human health, natural environment and natural resources. Three damage categories are distinguished: Human Health, Ecosystem Quality and Resources. Multiple endpoint indicators are combined in one single indicator measured in Eco-Indicator Points (Pt) to provide a robust assessment. Endpoint indicators represent the consequences of negative environmental effects on humans and ecosystems and are the "endpoint" of a possible chain of causes and effects. Damage category level is normalized depending on the chosen perspective. In the hierarchist perspective (chosen in this study) the chosen time perspective is long-term and substances are included if there is a consensus regarding their effect. One of the advantages of Eco-indicator 99 is the single score output (expressed in Pt) that enables a comparison of different components of a product/service or different products/services.

Problem-oriented methods, such as CML 2001 (JRC 2010), have midpoint effect categories and relevant indicators to model cases at an early stage in the cause-effect chain, namely translate effects into environmental themes such as climate change, acidification, human toxicity, etc., which allows a transparent assessment. This means that CLM indicators aggregate data on emissions (the starting points in the cause-effect chain) to potential effects in various categories (e.g. global warming, acidification, etc.), but do not assess the endpoints, such as the loss in terms of biodiversity, damage to human health, etc., caused by these effects (WRAP 2008). Each effect category is characterized by a midpoint indicator, which uses a defined reference substance in order to quantify the effect of a classified emission in relation to the reference substance. The CML method has different sets of normalization. The step of normalization calculates the magnitude of the effect category on the investigated system in relation to reference information (Guinée et al. 2002). CML provides detailed information about several environmental effect categories. The Global Warming Potential (GWP100) indicator, expressed in kg of CO_2-eq., is the indicator used from CML 2001, which is closely correlated with energy use (Blengini 2009), and is a measure of the Greenhouse Effect according to IPCC.

LCA implementation can be facilitated using relevant software and its corresponding effect assessment methods. In any case, the functional unit, boundary selection and limitations must be defined. It should be emphasized that the appropriate functional unit for LCA services within the hotel sector is more difficult to define than any other industry. The most common functional units used in similar studies are one "guest night" (Filimonau et al. 2011) , e.g. a night spent by one tourist in one ac-

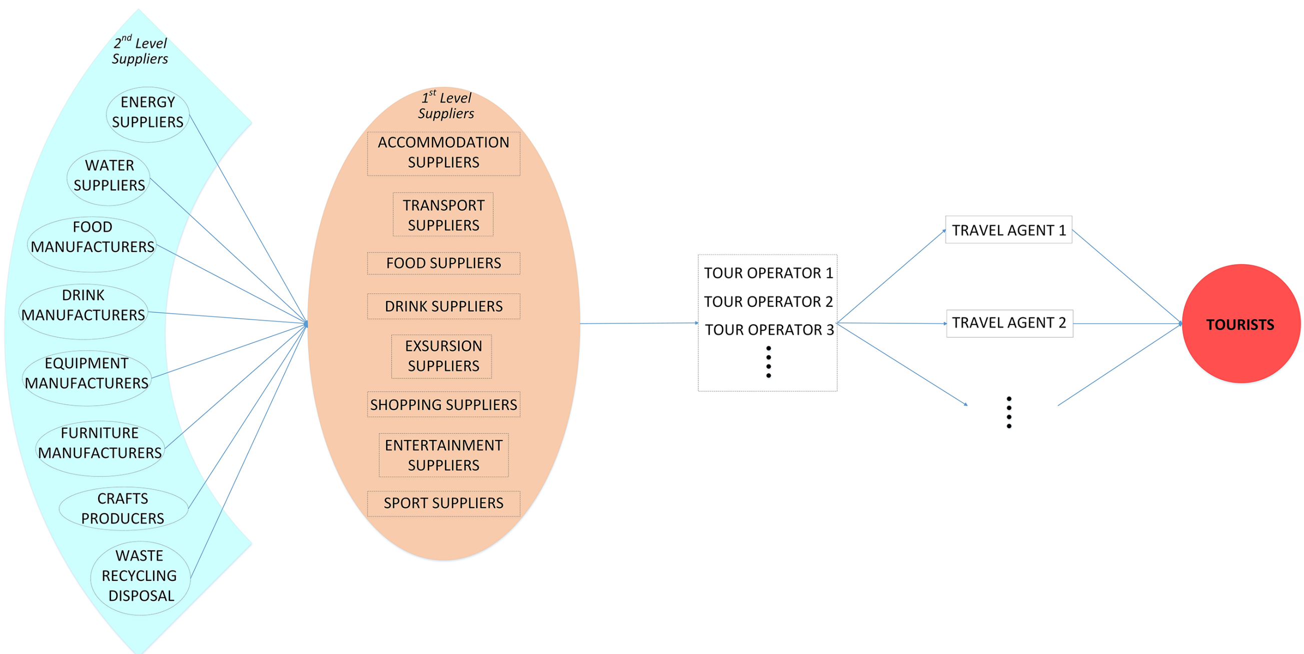

Fig. 1 Links in the overall TSC related to activities inbound/outbound in a DACT.

commodation building, and 1 week of a holiday including transport services to reach and leave the destination (Michailidou et al. 2016).

Case Study

The selected DACT for implementation of the proposed approach is Chalkidiki, a large peninsula in Central Macedonia with the longest coastline (550 kilometers) of all land prefectures in Greece. The nearest airport to Chalkidiki is the International Airport "Makedonia", close to the city of Thessaloniki. Chalkidiki has 511 1–5 star hotels, with a total of 44,579 beds, which is approximately 5% of the hotels nationally. With a total surface area of 2,900 km^2 and a population of 105,908 inhabitants in 2011, the number of international tourists was over 523,000 in 2012 (EL.STAT. 2014), which approximates to a 500% increase in population. In 2012, 80% of all tourists visiting Chalkidiki were international tourists, 49.2% of which came from 27 countries (excluding Greece) in the European Union (EU) and 49.6% from the rest of Europe (including Russia and Turkey). 34.2% of the tourists visiting Chalkidiki came from the Balkans and Romania, whereas tourists from Russia exceeded 27%. The area is characterized by high "tourism flows" compared to the permanent residents, and numerous agents of "dynamic" environmental burden, especially transport for reaching and leaving the destination and for recreational purposes.

After the selection of DACT, hotels were selected as the 1st level suppliers to be studied. In an effort to promote LCT principles and approach hotel managers in the area, a questionnaire was prepared. A pre-test procedure was conducted in order to assess the comprehensibility of the "draft" questionnaire and the probable effectiveness of extracting data from managers/directors/engineers. Essential introductory information was provided to the interviewees synoptically combined with a brief description of the principles of LCT and LCA, and managers gave their input regarding questionnaire's content based on their expertise. They participated in the process for establishing the main components in the implementation of the results of the LCA. Furthermore, they emphasized the need to keep the questionnaire simple and comprehensible. The pilot-study revealed that all hotel managers understood the input required. After making the appropriate modifications and improvements, the final questionnaire was produced.

For the case studied, SimaPro 8 software was used. The LCIA methods chosen are Eco-indicator 99 and CML 2001. The functional unit of the system studied is defined as one week of a holiday including transport services to reach and leave the destination. The system boundary is regarded as the operational use of a hotel including water and energy consumption for: (i) HVAC systems, (ii) production of hot water, (iii) lighting, (iv) kitchen operation, e.g. cooking appliances, refrigerators, freezers, etc., (v) laundry facilities and (vi) other electrical devices e.g. TV's, refrigerators in rooms, cleaning devices, and elevators. The transport of tourists from their original place to the hotel and their return is also taken into account. Waste generation is excluded from this study since the hotels studied did not keep such records, which is typical of the area studied. Two seaside large-sized hotels were examined in the area studied. The characteristics of each hotel are presented in Table 1.

Table 1 Characteristics of the two hotels studied in Chalkidiki (Reference year 2013).

	Hotel 1 (5*)	**Hotel 2 (3*)**
Location	Sithonia	Kassandra
No of Rooms/Beds	202/500	151/400
No of floors	2	2
Surface area	15,000 m^2	5,936 m^2
Seasonal operation	6 months	6 months
Occupancy rate	92%	94%
Type of building construction	separate standing	separate standing
Distance from airport	100 km	102 km
Fuel for Heating	Diesel	Gas
Fuel for Air Conditioning	Electricity	Electricity
Fuel for Hot Water	Diesel	Gas
Facilities & services offered	3 swimming pools, spa, 2 conference rooms	2 swimming pools, tennis, basketball & volley courts
Laundry	Yes	Yes
In-house restaurant	2 restaurants, bar, beach bar	1 restaurant, 2 bars
Year of construction	2007	1991

According to EL.STAT. (2014), 65% of international tourists in 2012 travelled by airplane to the International Airport "Makedonia" in Thessaloniki and then reached their hotel by coach or car. The remaining 35% of international tourists came from the Balkan Area and mainly came by car. For the road transport analysis, a petrol car EURO 4 with average occupancy of 3 passengers is assumed for tourists coming from the Balkans, whereas for the other tourists it is a coach for their transport from the airport and back. Flight distances from major airports near the capital of each country to International Airport "Makedonia" were calculated.

Results and Discussion

A fully detailed "network of activities" for each hotel was created in order to assess their overall environmental burden for two cases: (a) transport of tourists was not taken into account and (b) transport was taken into ac-

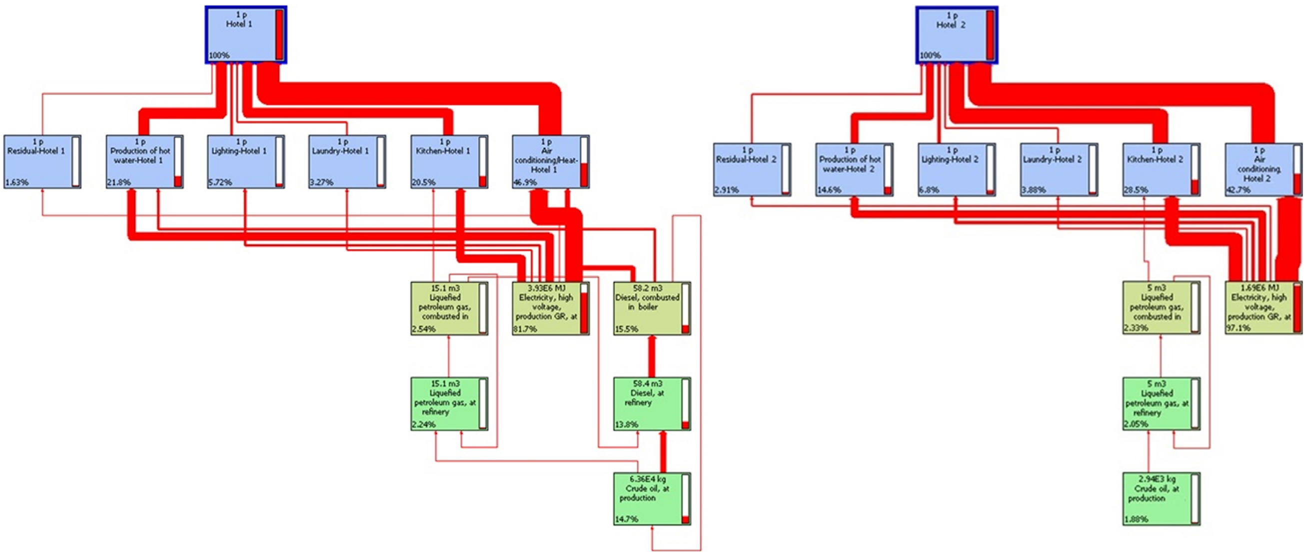

Fig. 2 Overview of the processes networks for hotels 1 and 2 generated in SimaPro 8.

count (Fig. 2). According to Eco-Indicator 99 effect assessment method for case (a), the operational use of hotel 1 resulted in greater environmental damage than that of hotel 2 (Fig. 3). When transport is included in the LCIA (case (b)), transport is responsible for the biggest share of the total environmental damage for both hotels. In addition, a comparative analysis of travel services in the case studied demonstrates that air transport has the highest absolute effect on all three categories of endpoints of Eco-indicator 99 (Resources, Ecosystem Quality, Human Health) compared to road transport. This finding is in line with the results of other similar studies, that airplanes are the most carbon intense means of transport (e.g. Filimonau et al. 2014).

Fig. 3 Evaluation of the effect of both hotels in terms of (a) operational use and (b) operational use, air and road transport, with Eco-indicator 99, expressed in MPt (=10^6 Pt).

When the operational phase of hotels is considered in isolation, HVAC systems are the biggest energy users in all cases, followed by kitchen facilities and the production of hot water. This is characteristic of all-sizes of hotels in Chalkidiki as solar energy, surprisingly, is not widely exploited in this area. Thus, most of the environmental loads of a hotels' operation arises from fossil fuel consumption (especially from lignite-based electricity). Based on these results, policy making should primarily put forward incentives for maximizing the use of Renewable Energy Sources (RES) by hotels in this area. Measures such as the use of energy-efficient lights in tourist lodgings, solar water heating systems and HVAC and lighting automation systems need to be promoted in order to minimize the overall environmental effect attributed to tourism in Chalkidiki. External wall insulation is also another important measure for saving energy especially for hotels that are more than 20 years old. These options highlight the need for central government initiatives to provide economic instruments and financial motives for both local authorities and tourism enterprises. These measures are easy to implement, have significant environmental benefit in relation to their cost and are socially very acceptable.

Fig. 4 illustrates the results of midpoint effect category scores for the two hotels, including transport. The effect on fossil fuel consumption is the highest for both hotels due to transport activities and use of conventional lignite electricity. Respiratory inorganics follow in terms of ranking of their effects relative to fossil fuel consumption. Effects on respiratory organics, radiation and ozone layer are negligible and are not presented in Fig. 4. The analysis demonstrates that hotel 1 is responsible for the largest share in terms of all 11 effect categories of Eco-indicator 99.

The effect assessment method CML 2001 was used to determine the midpoint effect category of Global Warming Potential over a period of 100 years (GWP100). Hotel 1 is responsible for the highest CO_2-eq. emissions (Fig. 5). Although both hotels are approximately the same distance from the airport, the difference in CO_2-eq. emissions is due to the different number of international tourists. A comparative analysis of travel scenarios demonstrates that air transport has the highest effect on all three categories of endpoints of Eco-indicator 99. This is in line with the results of other studies, that airplanes are the most carbon intense means of transport (e.g. Peeters and Schouten 2006).

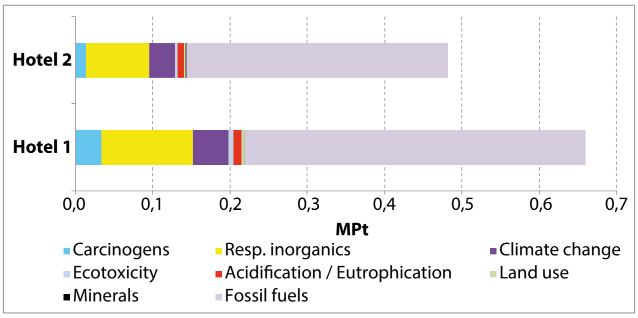

Fig. 4 Results of the effect category scores of Eco-indicator 99 for both hotels including transport.

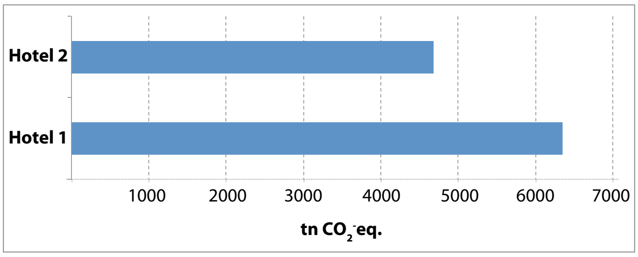

Fig. 5 100-year projection of the global warming potentials (GWP) in terms of CO_2 for each hotel.

Limitations

Although it is well established that the TSCM includes many components, accommodation and transport are the central factors of tourism, since they influence tourists' choices (Guo and He 2012). On this basis, this study initially was planned to gather data from all the suppliers of each hotel, whose manager agreed to participate, in order to assess the environmental effects of the TSCM of a DACT. Unfortunately, most of the owners or managers of the large hotels refused to participate in this study because they were not free to do so or feared the lack of confidentiality, despite written assurance from the researchers. In addition, most of them claimed they could not provide us with data regarding their suppliers without their consent. Collecting information from each supplier of each hotel is a difficult task. On the other hand, the majority of small hotels in Chalkidiki do not keep detailed records of their resource consumption. These are the reasons for restricting the study to the suppliers of energy and water to the hotels and transport for tourists.

Hotels with ecolabels and EMS certification facilitate the task of data collection for the LCIA, since they keep up to date records. It should be noted that hotel 1 has been awarded a Green Key. Large-sized hotels are more willing to adopt environmental management schemes in order to ensure that their services and products are environmental-friendly, since they possess the capacity and resources and have the ability to draw on appropriate expertise to introduce environmental protection measures (Ayuso 2007). To this end, large-sized hotels need to ascertain whether every component of the services they offer and products they buy from their suppliers are environmental-friendly, forcing suppliers/companies to engage with their downstream supply chain towards the consumer and their upstream chain towards producers. Large-sized hotels incorporate environmental awareness and efficiency as a product quality issue for their suppliers (Fond et al. 2008).

Conclusions

This paper clearly indicates that LCIA can form the basis for efficiently promoting GTSCM. The corresponding measures and strategies for tourism are driven mainly by industry's desire to reduce the risk of a negative public image and increase prospective organizational benefits (Budeanu 2009). The fundamental principle of GTSCM rests on collaboration between companies and their suppliers, and their willingness to link their aims and essential operational processes to create unique, international, market satisfying resources that will satisfy their customers and help them gain a competitive advantage. Through collaborative research and development, companies can develop more innovative, environmental products and services of higher quality with the assistance of their suppliers (Tan 2002).

Hotels are highly interdependent with other businesses, which provides a unique opportunity to encourage their partners to help them to attain their environmental mission (Lakshmi 2002). As hotel companies manage and operate their properties, they should focus on several aspects, such as logistics management, inventory management, information technology, procurement and distribution, lean and green supply chain practices. Focusing on the logistics and supply chain of an organization's operations has helped a wide variety of industries become logistic powerhouses as part of their operations performance. If applied properly by the hotel industry to improve efficiencies and reduce costs, hotel companies will not only save money, but also contribute to the greening of TSCM.

The accommodation sector is only a part of the TSC, all members/parts should manage their activities by considering their links with climate change and reducing their carbon-footprint, by taking into account the whole chain. Hotels should be very careful about their environmental management since unconscious and unplanned practices can cause weaknesses in the whole GSCM. The hospitality sector may also benefit from applying some of the lessons learned from the application of GSCM practices in manufacturing and other sectors. The collection of data across the supply chain of these two hotels and other hotels in the area is definitely a challenge for the future if the environmental loads and greenhouse gas emissions of the whole TSCM are to be assessed and specific recommendations for minimizing environmental loads and greenhouse gas emissions proposed.

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EVALUATION OF WATER SAVING MEASURES FOR MID-SIZED TOURIST LODGING UNITS: THE CASE OF SAMOS ISLAND, GREECE

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ABSTRACT

Hotel sector causes significant environmental stress in both natural and built up areas due to their consumption of water and energy. In addition, the production of large volumes of liquid and solid waste results in a significant environmental footprint. The use of water and energy by hotels is strongly linked (e.g. energy is consumed for hot water, operation of the pool, preparation of meals, etc.) and usually referred to as the water – energy nexus. Thus, for big consumers like hotels, water and energy consumption should be addressed collectively as water-saving measures can lead to a reduction in energy consumption. The aim of this study is to assess the environmental performance of mid-sized hotel units by analyzing and quantifying their use of water. An analysis using a two-step approach was made of 8 accommodation facilities located on Samos Island, Greece: (i) a mapping of water use by adopting an end-use approach, and then (ii) an assessment of saving practices using three main criteria: savings, cost of investment and payback time. The preliminary results indicate that for small sized lodging units, water consumed inside the guest rooms accounts for the majority of all the water used and low-cost water saving measures and actions can reduce the pressure on water resources without disturbing guests, while increasing the financial profitability of a hotel.

Keywords: tourist lodging mid-sized units, water uses, saving potential, Samos Island

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Introduction

More than 30% of international tourist destinations are located within the Mediterranean basin, which makes it among the most popular of tourist areas globally. The tourist industry in the Mediterranean region has traditionally been characterized by strong seasonality, with large variations in occupancy rates between winter and summer. Climatic factors, such as temperature, sunshine hours and precipitation mainly determine the flow of international tourism within Europe, which impose tremendous pressures on the natural resources of a region (Amelung and Viner 2006). In 2007, Bohdanowicz and Martina conducted a survey of a large number of Hilton International and Scandic Europe hotels in order to establish energy and water consumption benchmarks and classify them. In order to obtain representative indicators, components such as brand name, hotel standards, resource management, environmental performance, location, and climate conditions were considered. In addition, water management based on reducing-reusing-reaching-recycling approaches (Kasim et al. 2014) and a tourism environmental composite indicator – TECI (Michailidou et al. 2015) were recently developed to propose good practices for hotel managers on how different sized hotel units could implement various water savings measures that they were intellectually and technologically capable of.

Lodging operations can be characterized as successful and efficient as long as they provide the right mix of characteristics to attract and retain guests. Two decades ago, the lodging factors considered to determine the quality of a tourist lodging unit, were primarily: facility features, room amenities, housekeeping, security and food-service operation (Griffin 1998). Nowadays, a significant portion of the potential visitors are looking for something that will improve their hotel stay by providing top-level environmental-friendly services.

Mass tourism activities and lodging units can lead to degradation of the natural environment by putting pressure on vulnerable natural resources such as water and soil. Crete, Rhodes and Corfu are among the most well-known tourist destinations in Greece, where large sized tourist units are operating to accommodate the increased loads mainly during summer. On the other hand, in most small and recently developed tourist areas like the Greek islands in the Aegean Sea, local businesses are attempting to reduce the negative social-economic and environmental effects of mass tourism by promoting actions that will increase the added value of their local tourist product. For this reason, small and mid-sized tourist lodging units are encouraged by the local commercial and tourist chambers to invest in high quality tourist services in order to increase their environmental profile for those tourist groups that are interested in knowing the significant advantages of the local physical and cultural

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environment. Therefore, the successful implementation of water saving practices in small sized hotels should be encouraged since it contributes to tourism sustainability (Barberan et al. 2013) and could attract specific groups of tourists that are willing to pay more for eco-friendly facilities.

Exploitation of the energy saving potential of hotel infrastructures usually requires a large investment, however, wherever advanced Energy Efficiency Measures (EEMs) have been implemented, there have been significant energy savings (Chedwal et al. 2015). Interventions related to energy saving equipment and use of renewable energy sources are among the practices that tourists are increasingly looking for and are willing to pay for in hotels (Tsagarakis et al. 2011). Efficiency in water consumption is an important factor in the evaluation of hotel sustainability; however, it still of low priority. Barberan et al. (2013) show that a small investment in water saving practices could lead to a significant reduction in water consumption and its associated operating costs. In most of the energy-consuming activities in a hotel (e.g. swimming pool, meal preparations, laundry), water is also used, so the water-saving measures can lead to energy saving as well.

In this paper, an analysis of the water saving potential of lodging units is attempted. The approach includes the following steps:

(i) mapping of water use by adopting an end-use approach,
(ii) assessment of saving practices using three main criteria: savings, cost of investment and payback time.

The large number of activities taking place in a hotel that increase water consumption were taken into account, in order to provide hotel owners and managers with a detailed picture of their current water consumption. By applying a tool that calculates the reduction in the operational cost after the implementation of water saving measures, a clear view of the economic benefits of investing in water and energy efficiency was obtained.

Methodological Approach

The analysis focused on eight mid-sized lodging units, located on the island of Samos in Greece. This type of accommodation is very common on Greek islands. They are primarily small family businesses that appeal to medium-income tourists as they offer high quality services mainly benefiting from the natural environment and the cultural heritage of Greece. In order to enhance their environmental image, the units analyzed expressed an interest in investing in rational water management, which will reduce their operating costs and enhance their environmental image. The "unit use" approach (Froukh 2001; Davis 2003) is used to estimate water demand, using Eq. 1 and Eq. 2:

$$Q = \sum_{u=1}^{n} q_{u,t} N_{u,t} \quad (1)$$

$$q_{u,t} = \sum_{i=1}^{m} f_{i,t} T_{i,t} c_{i,t} \quad (2)$$

Where:

Q is total water demand,
$q_{u,t}$ is average water used per unit and time for a specific use (u) at a specific time (t),
$N_{u,t}$ is number of units used at time t,
$f_{i,t}$ is frequency with which the appliance i is used per day,
$T_{i,t}$ is average time for which the appliance i is used per day,
$c_{i,t}$ is consumption of appliance i in terms of liters of water per day.

Water demand includes four main water uses: (i) hosting customers, (ii) pool, (iii) garden irrigation, and (iv) other services and uses (washing of towels/linen, cleaning, use of employees and visitors, preparing light meals). The estimates are based on water use devices that are already installed in a lodging unit and their use (frequency). Water leakages are also taken into account in order to have a more representative estimate of water demand. The list of the data needed for this analysis is in Table 1.

Table 1 List of the data needed for estimating the water demand of hotels.

Unit characteristics	– Unit type (hotel, apartment, villa) – Number of rooms – Number of beds – Services provided (e.g. breakfast, pool, linen washing) – Garden features – Number of employees – Number of visitors
Occupancy	– Number of beds (monthly) – Number of nights (monthly)
Water equipment	– Pool capacity – Irrigation system – Equipment type and frequency of use – Leakage %
Related costs	– Tiered water invoice – Pricing of sewerage services (fixed fee, a percentage of the value of water consumed)

For the purpose of this analysis, an application tool was developed that took into consideration the water saving technologies and operation options (Table 2) that could be easily implemented in a mid-sized lodging unit. The analysis involves four steps:

- Step 1 "Mapping of water uses": Data entry concerning the type of facility, number of visitors, existing appliances, frequency of use, etc.
- Step 2 "Estimation of water demand": Monthly and annual water demand for the four main water use categories (hosting customers, pool, garden irrigation, other services and uses).

- Step 3 “Selection of water saving options”: Selection of water saving technologies and options and data entry concerning their cost.
- Step 4 “Comparative assessment of water saving options”: Assessment of each technology using three criteria: (i) water saving potential, (ii) water cost reduction, and (iii) payback time.

Table 2 List of water saving technologies available for each of the water uses in a lodging unit.

Hosting customers	– Use of dual flash toilets – Use of low flow appliances – Use of recycled water in the toilet – Leakage control
Pool	– Filling with sea water
Garden	– Change from irrigation to efficient technologies – Rainwater harvesting for irrigation – Use of recycled water for irrigation
Other services	– Replacement of linen every three days – Replacement of washing machines with water and energy efficient appliances – Use of dual flash toilets – Use of low flow appliances

Test application

The water use profile of eight accommodation facilities (seven hotels and one block of apartments) was analyzed. Four of them operated on a seasonal basis (May to October) and the other four on an annual basis. Most of the units (5 out of 8) are small-medium with less than 60 rooms. The services provided include breakfast (7 out of 8 units), pool (8 out of 8 units), linen washing in the unit (8 out of 8 units) and hosting events and meetings (5 out of 8 units). Seven of the units have an irrigated garden.

The data collected for 2015 were analyzed (i.e. occupancy, number of employees, water equipment), whereas the values of specific parameters were obtained from national legislation (e.g. irrigation requirements per type of plant, irrigation efficiency, Source: JMD F16/6631/89) or the literature (e.g. water use rates of appliances, water demand of different type of washing machine, source: www.watersave.gr). The parameter values used in the calculations are presented in Table 3.

Table 3 Water consumption of a hotel when operational (typical values).

Irrigation method Source: JMD F 16/6631/89	**Efficiency**	
Inundation	0.70	
Sprinklers	0.85	
Furrow	0.68	
Drip	0.94	
Vegetation	**Water consumption**	
	(m^3/day)	**(m^3/week)**
Lawn	0.008	0.0056
Bush	0.004	0.008
Trees	0.016	0.016
	Washing machine (liters/kg of linen)	**Dishwasher (liters/per cycle)**
Economy	7	20
Medium	10	30
Large	12	40
Appliance	**Type**	**value**
Shower	High flow (l min^{-1})	15
	Low flow (liters/flush)	6
Toilet flush	Single flush (l min^{-1})	9
	Double flush (l min^{-1})	6
Sink tap	High flow (l min^{-1})	10
	Low flow (l min^{-1})	5
Bathroom tap	High flow (l min^{-1})	12
	Low flow (l min^{-1})	7
Kitchen sink tap	High flow (l min^{-1})	8
	Low flow (l min^{-1})	6
Water consumption for breakfast preparation (l/guest/day)		
Breakfast preparation	10	
Breakfast preparation and washing	15	

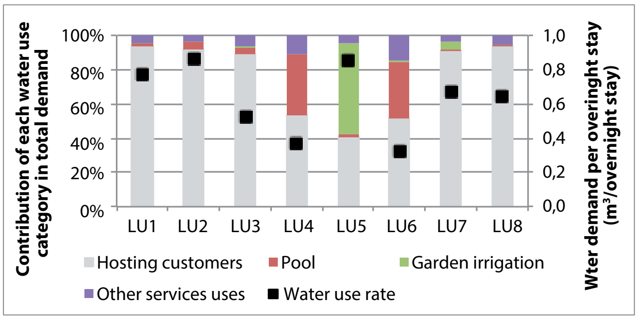

Fig. 1 Water use prolife of the accommodation units examined.

In Fig. 1 the water use profile of the hotel units selected is presented. As has been estimated from the collected data (Step 2: estimation of water demand), water use rates per overnight stay are in the range of 0.32 to 0.86 m^3/overnight stay. In six out of eight units the average water use rate exceeds 0.40 m^3/overnight stay, which is a typical average for tourism (Gössling et al. 2012), while the lowest water use rate was estimated for establishments that have already installed low flow and water efficient appliances. May is the month with the highest water demand as is that month that the pools are filled with water.

Results indicate that the water use profile of the units investigated is well represented by the difference between the actual (measured) and estimated water use, which is small and ranges from 1.1% to 5.3%. In order to assess the water saving potential of the twenty water saving measures, which are described below, they were included in the calculation tool and analyzed:

- Hosting customers component
  1. Replacement of the regular shower heads with water saving systems
  2. Replacement of regular taps with water saving systems – bathroom sink
  3. Use of a flow controller on the taps – bathroom sink
  4. Replacement of regular taps with water saving systems – bathroom tap
  5. Replacement of existing units with dual flushing toilets
  6. Leakage control
  7. Recycle of water for toilet use
- Pool
  8. Use of sea water in the swimming pool
- Garden irrigation
  9. Change the irrigation method (drip irrigation) – grass
  10. Change the irrigation method (drip irrigation) – bush
  11. Change the irrigation method (drip irrigation) – tree
  12. Rainwater harvesting for irrigation
  13. Recycle water for irrigation
- Other services and water uses
  14. Use towels for more than one day
  15. Use the same bed linen for three days
  16. Washing machine replacement
  17. Dish washer replacement
  18. Replacement of regular taps with water saving systems – bathroom sink
  19. Use of a flow controller on the taps – bathroom sink
  20. Replacement of the existing units with dual flush toilets

Table 4 Characteristics of two of the lodging units in the sample.

Hotel ID	LU6	LU7
Operation	Seasonal (May–October)	Annual
Number of rooms	43	46
Number of employees	11	8
Annual value of overnight stays	5563	15000
Pool size (m^3)	600	100
Garden – lawn (area)	No	Yes (300 m^2)
Garden – trees & bushes (number)	18	19
Irrigation efficiency	0.7	0.7
Linen washing	Yes	Yes
Use of low flow/water saving appliances	Yes	No
Estimated water use rate (m^3/overnight stay)	0.32	0.67

The characteristics of the two lodging units that were sampled (lodgings) in this study are presented in Table 4.

Table 5 presents the water saving potential of the technologies tested. The range of values represent the differences in the water use profile and the type of appliances that are already being used in each lodging unit. As expected, there is a significant reduction in water demand by improving water use efficiency for hosting customers (in the rooms) and garden irrigation.

Table 5 Water saving potential per water saving technology.

Water saving technology	Saving potential (%)	Water saving technology	Saving potential (%)
M1	10.537 to 21.423	M11	0.004 to 0.061
M2	6.885 to 26.414	M12	0.019 to 26.570
M3	2.754 to 10.565	M13	0.019 to 26.570
M4	2.738 to 15.869	M14	0.008 to 0.062
M5	1.773 to 3.562	M15	0.018 to 0.137
M6	5.000 to 5.100	M16	0.112 to 3.051
M7	2.659 to 5.564	M17	0.037 to 0.075
M8	0.681 to 33.342	M18	0.119 to 1.106
M9	0.864 to 9.372	M19	0.068 to 0.632
M10	0.001 to 0.052	M20	0.171 to 1.581

Fig. 2 presents the average values and range of savings expressed in Euros obtained by using the different water saving technologies. Differences are attributed to different water use profiles and technologies for each lodging unit. It should be noted that even though M12 and M13 result in similar reductions in the water bill, the payback time is different as the cost for the implementation of each technology varies. As a result, M12 has a significantly lower payback time (~5 times less).

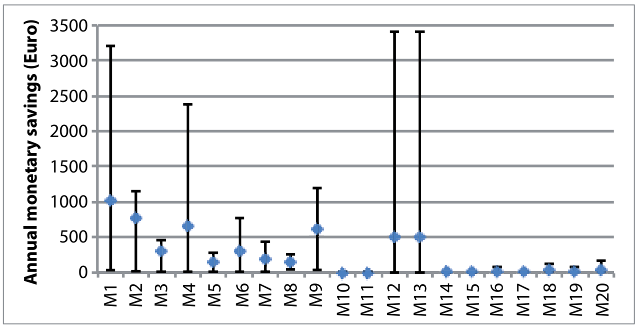

Fig. 2 Water use prolife of the accommodation units examined.

Finally, in Fig. 3 is the predicted water demand of the two lodging units if they used the different water saving measures.

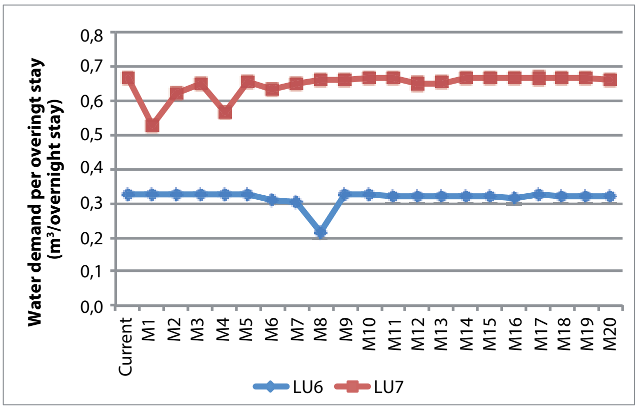

Fig. 3 Water demand per overnight stay in the two lodging units when using the different water saving measures.

Discussion and Conclusions

In this paper, a preliminary analysis of the water saving potential of a group of mid-sized lodging units was carried out in order to define the water uses that mainly contribute to their water consumption and provide an insight for hotel managers of the benefits associated with environmental friendly practices. A clear understanding of the consumption profile of each unit was obtained, which is determined by the geographical location and climate in the region.

Even though the results are only for a small group of units, there are several conclusions that can be drawn. For this type of lodging unit, guest rooms (hosting services) are the main water-consuming factor, which is contrary to Gössling et al. (2012) conclusion, who report that the main water-consuming factors, in general, are irrigated gardens, swimming pools, spa and sports facilities, golf courses, cooling towers (if any), guest rooms and kitchens. This is possibly due to the fact that even though most of the units investigated have gardens, they are relatively small compared to those of most large hotels. Another important finding is the fact that a significant reduction in water consumption can be achieved by using sea water instead of freshwater in the swimming pools. This is a practice that is not typical in Greece but could result in significant savings and reduction in the demand for water on the islands. Summarizing, the presented results are in accordance with those of Barberan et al. (2013), who propose that investment in low cost water savings measures and actions can reduce the consumption of water without inconveniencing guests while increasing the financial profitability of a hotel.

The Eastern Mediterranean is among the most vulnerable regions in terms of the increase in water consumption associated with the increase in tourism in time and space, which is putting a tremendous strain on domestic fresh water supplies and infrastructure. In popular tourist resorts, it is especially important to estimate both direct and indirect water consumption in order to achieve a sustainable consumption (Hadjikakou et al. 2013). In places where the main fresh water resource is groundwater (Gatt and Schranz 2015), as on islands like Malta, Crete and Cyprus, additional efforts should be made to use water in a sustainable way.

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PASSIVE SAMPLING OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS IN AQUATIC ENVIRONMENTS

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ABSTRACT

Passive sampling is a rapidly developing technology, which is widely used for the monitoring of pollutants in different environments. Passive sampling offers significant advantages over traditional grab sampling. In the present review, the authors summarize the current literature on the methods of passive sampling used in the environmental monitoring of polar or semi-polar compounds in aqueous matrices. Methods of calibrating, design and deployment of samplers are also discussed. A major focus of this review is the use of polar organic compound integrative samplers (POCIS) and their use in sampling and monitoring of pharmaceuticals and personal care products (PCPs) in both equilibrium and non-equilibrium conditions.

Keywords: passive sampling, polar organic chemical integrative samplers, aquatic matrices, pharmaceuticals, personal care products

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Introduction

Since its invention more than four decades ago, passive sampling has been widely used for the purpose of environmental monitoring in different media (e.g. soil, air, sediments and water). Despite its relatively long history (first use of passive sampling is reported in 1980s (Palmes and Gunnison 1973; Fowler 1982; Rose and Perkins 1982)), passive sampling is still developing and there are numerous review articles on this topic. Historically, passive sampling based on the principle of diffusion dosimeters was used for monitoring toxic chemicals in workplaces (Palmes and Gunnison 1973). Pine needles are one of the first "passive sampling devices", whose analysis is a well-established method for monitoring organic chemicals in the air (Kylin et al. 1994). Some organisms may also serve as "passive samplers" in the aquatic environment. They are sometimes called biological "dosimeters" and can be used as an indicator of the level of contamination in the aquatic biosphere (Schilderman et al. 1999).

The monitoring of trace levels of organic contaminants in water bodies is an ongoing challenge and has become possible only recently due to significant improvements in analytical techniques. Many of the environmental contaminants, often called 'emerging contaminants', are polar or semi-polar compounds such as pharmaceuticals and personal care products (PCPs). Thus, the behaviour and fate of these pollutants in the environment can be very different from the previously studied persistent organic pollutants (e.g. polychlorinated biphenyl or polyaromatic hydrocarbons). Contaminant concentrations can vary substantially because of the spatial and temporal variability of the source, pathways of its sorption and desorption and the pattern of its degradation and dissolution. Also, biogeochemical processes and human activities can influence the concentration of pollutants at point sources. Generally, the assessment of pollution is based on concentrations determined by analytical methods and/or toxicity data and biological methods. This means that in order to assess the quality of the environment, a large number of samples has to be analyzed to determine daily, monthly and/or annual time-weighted average concentrations (TWA) of the pollutants of interest. This monitoring approach can be prohibitively expensive and, depending on the technique used, can also very often be unfriendly to the environment.

Passive sampling, as a low-tech and cost-effective technique, represents a promising monitoring tool, which could avoid almost every disadvantage of active sampling and/or of the methods of preparing the samples. As an analytical tool, passive sampling is used to achieve some of the most basic steps in preparing samples. These could include pre-concentrating the analytes in order to increase the detection limits during measurements, reducing or eliminating solvent consumption (green chemistry) and elimination or reduction of matrix interferences. In most cases, passive sampling greatly simplify sample collection and preparation by eliminating training for device handling, need for power sources for their operation, provide a significant reduction in the cost of analysis and protection of analytes during transport and storage. Furthermore, many passive samplers can easily provide TWA concentrations, which is hardly achievable using active methods of sampling.

The first passive sampling of liquid media was used to monitor dissolved inorganic compounds in the surface water in an enclosed dialysis membrane (Benes and Steinnes 1974). First use of semi-permeable membrane devices (SPMDs) for sampling organic compounds was reported in 1990s (Huckins et al. 1990). Since then, many passive sampling devices have been developed and many of them are currently available commercially. Designing of passive samplers and their application in environmental analysis are described in several reviews (Vrana et al. 2005; Kot-Wasik et al. 2007; Seethapathy et al. 2008; Zabiegala et al. 2010). However, there are still very few publications on the use of passive sampling for determining pharmaceuticals and personal care products (see Fig. 1).

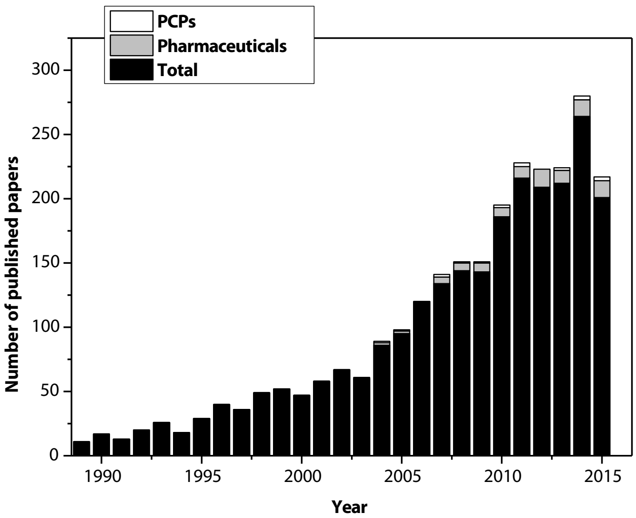

Fig. 1 Number of articles published on the application of passive sampling in aquatic environments between 1989 and 2015 with the number that focused on personal care products (PCPs) and pharmaceuticals indicated at the top of the figure.

In passive sampling, there are numerous variables that need to be considered (e.g. form of the analyte(s) of interest, duration of sampling, environmental parameters, chemical and physico-chemical properties of the analyte(s), medium or matrix to be sampled, type of measurement, whether quantitative or semi quantitative, cost and availability etc.). Moreover, there are often situations when a combination of passive samplers need to be deployed in order to obtain the relevant data. The physical deployment of passive samplers is simple but the sampling strategy involved can be more complicated and should therefore include correct assessment of the type of passive sampler or combination thereof; the exact location, time and durations of exposure and the analytical assessment. Knowledge of the type of pollution, its source, its potential fate in the environment together with the deployed analytical methods and their limitations are also important factors that need to be considered for a proper interpretation of data.

Passive sampling mechanisms are fairly well described for non-polar compounds (e.g. polychlorinated biphenyls, polyaromatic hydrocarbons, pesticides) but the mechanisms involved in sampling polar compounds are not fully characterized in terms of modelling of the uptake rates and various other effects of environmental factors.

Passive Sampling

Types of Passive Samplers

Passive sampling can be defined as any sampling technique based on the free flow of analytes from the sampled medium to a receiving phase in a sampling device, which results from a difference between the chemical potentials of the analyte in the two media under consideration (e.g. water and sorbent). The type of information obtained from passive sampling depends, to a large extent, on the regimes in which passive samplers operate during exposure in the field. There are two types of passive sampling devices, samplers in which target analytes dissolve (e.g. absorption) and those in which analytes are adsorbed (e.g. surface bonding); but the sampling process is very similar in both types of sampler. Once they are exposed to water, accumulation of analytes in the receiving phase occur by diffusion through a static layer of water in well-defined openings in the case of diffusion samplers, or by permeation through a porous or non-porous membrane in the case of permeation samplers.

1. The first type of sampler is also referred to as a partition sampler because it is based on partition theory. These samplers can achieve equilibrium between the sampler and the media if they are exposed for long enough. The material used in the partition passive sampler is selected in such a way that the test compounds dissolve in it much better than in water and therefore become highly concentrated and, as a result, are easier to measure. Partition samplers are often called hydrophobic samplers because they are generally used for non-polar compounds. Thus, these devices rely on the diffusion of the compounds to reach equilibrium between the sampler and the water.
2. The second type of sampler is known as an adsorption sampler. In this case, compounds bond very strongly to the adsorption material present in the sampler. Sorption capacity of the material in the sampler is usually very high, thus no equilibrium is reached. Samplers often bond polar compounds very strongly and are therefore frequently referred to as polar samplers or kinetic/sink samplers. Thus, these devices rely on diffusion and sorption to accumulate compounds in the sampler and remove and accumulate the compounds from water during the deployment period.

The transport of target analytes from water to both types of passive sampler is diffusion-controlled, so that only freely dissolved substances are taken up or adsorbed and the variables in the uptake process for partition samplers are well known. The amount taken up by the partition sampler can therefore be used to calculate the concentration in the water phase. However, there are still a number of uncertain factors involved in the uptake process with regard to adsorption samplers and so there are also more uncertainties involved in the calculation of the concentration of analytes.

Whether a passive sampler is used in an equilibrium or non-equilibrium/kinetic mode also depends on:

– The exposure time of the passive samplers
– The concentration of target analytes
– The partitioning properties of target analytes
– The type of data that is to be obtained

Principles of Passive Sampling

Analytes in both types of samplers are trapped or retained in a suitable medium within the passive sampler, known as a reference or receiving phase. The receiving phase can be a solvent, chemical reagent or a porous adsorbent, which is exposed to the water phase during the sampling period. Dissolved analytes are not quantitatively extracted during the extraction process, but their adsorption or absorption generally follows the pattern shown in Fig. 2. The kinetics of exchange between a passive sampler and the water phase can be described by a first-order, one-compartment mathematical model:

$$C_s(t) = C_W \frac{k_1}{k_2}(1-e^{-k_2 t}),$$

where $C_s(t)$ is the concentration of the target analyte in the sampler at exposure time t, C_w is the concentration of the target analyte in the aqueous environment (TWA – the time-weighted average concentration of pollutant in the water phase), and k_1 and k_2 are the uptake and offload rate constants, respectively. Both main accumulation regimes, either kinetic or equilibrium, can be distinguished during the operation of the sampler in the field.

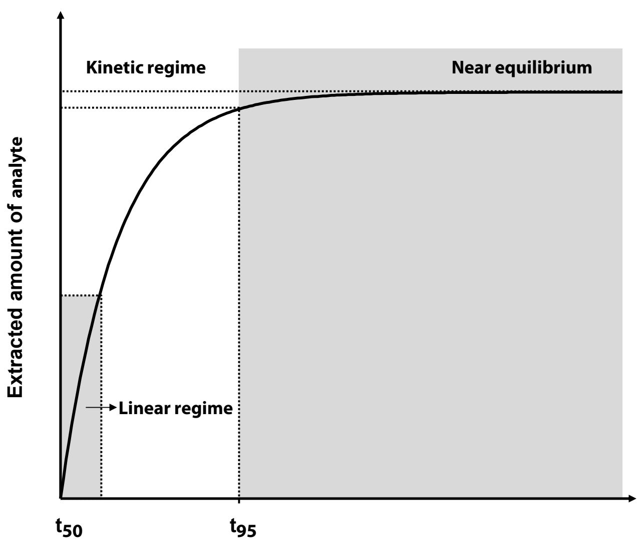

Fig. 2 Passive sampling devices operate in two mail regimes – kinetic and equilibrium.

Equilibrium Passive Samplers

In equilibrium passive samplers, the exposure time is sufficiently long to establish thermodynamic equilibrium between the matrix (reference/receiving phase) and water. Equilibrium could be reached within seconds to months depending on the sampler, the compound and its concentration. The equation can be reduced to:

$$C_s = C_W \frac{k_1}{k_2} = C_W K$$

In this equation K is the phase-water partition coefficient. The basic conditions of the equilibrium sampling technique is a known response time, after which a stable concentration is reached, and sampler capacity, which must be kept well below that of the sample to avoid depletion during extraction. The device response time should be shorter than any fluctuation in the sampled/sampling environment so that many environmental stressors do not effect the results.

The sampling times of different passive samplers range from seconds to months. The results obtained from equilibrium samplers are comparable with those obtained by grab sampling and therefore the device is not suitable for the determination of TWA concentrations (Kot-Wasik et al. 2007). Equilibrium passive samplers are often referred to as biological “dosimeters” (e.g. mussels, fish), because they mimic the part of the animal body where bioaccumulation and bioconcentration occurs. Samplers contain a receiving phase in which the contaminants are trapped as in living organisms. Equilibrium samplers provide the information about the level of contamination in the monitored environment instead of quantitative information on the concentration of pollutants.

Commercial products available:

– Regenerated-Cellulose Dialysis Membrane Samplers
– Nylon-Screen Passive Diffusion Samplers (NSPDS)
– Passive Vapor Diffusion Samplers (PVDs)
– Peeper Samplers
– Polyethylene Diffusion Bag Samplers (PDBs)
– Rigid Porous Polyethylene Samplers (RPPS)
– Diffusive Multi-layer Sampler (DMLS)

Passive samplers in equilibrium mode are used for monitoring DDT, Hg ions, chlorophenols, hexachlorobenzene, PCBs, anilines, pesticides, phenols, triclosan, PBDEs, biotoxins and PCDD/Fs (review in (Vrana et al. 2005; Kot-Wasik et al. 2007; Mills et al. 2007; Verreydt et al. 2010; Zabiegala et al. 2010; Lydy et al. 2014; Mills et al. 2014).

Kinetic Passive Samplers (Non-Equilibrium)

Non-equilibrium/kinetic passive samplers do not reach equilibrium with the surrounding environment within the sampling period. Kinetic sampling permits the measurement of analyte concentrations over extended periods of time. In kinetic sampling, the rate of mass transfer to the receiving phase is linearly proportional to the difference between the chemical activity of the target analyte in the water phase and in the reference phase. The rate of desorption of target analyte from the receiving phase to water is negligible and during the period of exposure the initial rate of uptake of the sampler is linear. The equation can be reduced to:

$$M_s\,(t) = C_W R_S t,$$

where $M_S\,(t)$ is the mass of target analyte accumulated in the receiving phase after a certain exposure time (t) and R_S is the proportionality constant – sampling rate. R_S may be interpreted as the volume of water cleared of analyte per unit exposure time by the device. R_S is usually not affected by C_w (the time-weighted average pollutant concentration in water phase), but can vary with water flow or turbulence, temperature and biofouling.

Kinetic samplers are characterized by high capacity for contaminants of interest. The high capacity ensures the continuous sampling throughout the exposure period. These samplers provide the TWA concentrations – concentration of target analytes in the sample matrix averaged over a known period of time.

Commercially available samplers:
- Polar Organic Chemical Integrative Samplers (POCIS) for VOCs
- Semi-Permeable Membrane Devices (SPMDs) for lipophilic organic compounds
- GORE™ Sorber Module
- Passive In-Situ Concentration Extraction Sampler (PISCES)
- Solid Phase Microextraction (SPME)
- Membrane-enclosed Sorptive Coating Sampler (MESCO)

Passive samplers in the kinetic mode have been recently used for monitoring DDT, endocrine disruptors, various pharmaceuticals, pesticides, personal care products, PAHs, PCBs, UV filters, plasticizers, organotin compounds etc. (review in Vrana et al. 2005; Kot-Wasik et al. 2007; Mills et al. 2007; Verreydt et al. 2010; Zabiegala et al. 2010; Harman et al. 2012; Amdany et al. 2014b; Lydy et al. 2014; Mills et al. 2014).

Factors Affecting Passive Sampling

The sampling rate is an important issue when linear (kinetic) uptake passive samplers are used for field sampling. Temperature, rate of water flow, salinity, pH and biofouling as well as the properties (e.g. K_{ow}) of some analytes are known to affect uptake. However the sampling rate could be a-priori determined in the laboratory during calibration or predicted by empirical equations and many parameters may have an important influence on it (Ouyang et al. 2007; Seethapathy et al. 2008).

Only analytes dissolved in the water can pass, by diffusion, the water boundary layer (WBL), which is generated due to the high viscosity at the surface of the sampler (Booij et al. 1998) and represents a rate-limiting step in the uptake into the receiving phase (except biofouling). The thickness of WBL is dependent on water flow or turbulence around the sampler and also depends on the type and properties of the membrane. These factors can significantly influence the rate of accumulation as is reported for non-polar samplers (Booij et al. 1998). After they cross the WBL analytes are transported across the membrane through the water-filled pores or via the polymer itself.

Finally, compounds are transferred to the sorbent material mainly via adsorption (polar substances) or absorption (non-polar substances). When water turbulence is high enough to make the resistance to mass transfer into the boundary layer negligible, transport through the membrane becomes the rate-limiting factor.

The influence of salinity and pH on R_S is usually compound-specific and highly dependent on the various chemical groups present in the structure of the analyte. Increasing salinity increases the energy required for a solute's molecular cavity to form and increases the partitioning of neutral compounds toward non-aqueous phases. This is also called salting-out and it increases with the size and decreases with the polarity of the analyte (Endo et al. 2012). Similarly, the pH will affect the R_S depending on the type of analyte, especially for basic analytes (Li et al. 2011). In several studies, very small effects of the water temperature is reported in the range of 5–25 °C (twofold or less) (Li et al. 2011). Biofouling is the accumulation of microorganisms and various flora and fauna on wet surfaces, which may form a biofilm. For extended exposure (e.g. POCIS samplers), biofouling of the surface can influence the mass transfer by increasing the thickness of the barrier on the membrane and also by blocking the water-filled pores (Huckins et al. 2006). The thickness of the biofilm varies from exposure to exposure and also between spots on the same membrane and the effect, is thus, difficult to predict. The problem of biofouling of the membrane can be reduced by using suitable membrane materials. POCIS samplers made of polyethersulphone slowly bleed anti-fouling solvent (e.g. hexane) during exposure and as a consequence are less affected by biofouling (Alvarez et al. 2004).

Calibration of Passive Samplers

There are several different calibration methods for determining the sampling rate (R_S) that vary in their level of complexity. Therefore, selecting the appropriate method depends on the research objective. Laboratory calibration is more often used than calibration *in situ*. However, calibration in the laboratory is a time-consuming procedure and it is impossible to encompass the wide range of environmental exposure conditions. Therefore a performance reference compound (PRC) is often used for calibration. The most often used calibration methods are:

- Static renewal – exposure of samplers to a small volume of fortified water, refreshed periodically to minimize the decrease in analyte concentration. The mass of the absorbed analyte is measured at intervals (Alvarez et al. 2004).
- Static depletion – exposure of samplers to single spiked (fortified) water and analysis of the analyte present in the water phase. Usually a high initial concentration is used and the depletion is monitored over several orders of magnitude (Bartelt-Hunt et al. 2011).
- Flow-through systems – exposure of several samplers in a tank filled with fortified water, which is continuously supplied. Samplers are removed from the tank over time and sorbents are analyzed in order to assess analyte uptake (Vrana et al. 2006).
- *In situ* calibration – measurement of sampling rate at the exact location where the sampling experiments are to be conducted. Deployed samplers are calibrated by comparing analyte accumulation with TWA concentration in water obtained from gram sampling (Harman et al. 2011).
- PRC based system – PRC are organic compounds that are introduced into the receiving phase of the sampler before it is exposed. PRC allows assessment of whether analytes are in equilibrium or in the kinetic phase and an estimate of R_S of the target analyte *in situ* as their dissipation shows isotropic kinetics analogous to analyte uptake (Booij et al. 1998).

Biomagnification

One of the major advantages of passive samplers used in equilibrium mode is that these devices can be used for determining biomagnification due to their similarities with biological systems (hydrophobic depots covered with a semi-permeable membrane). Thus the hydrophobic analytes are trapped in the receiving medium after the exposure of the device, as in living organisms. Sampling of indigenous or transplanted organisms (e.g. fish, microalgae, mussels) is an accepted practice in many programs focused on the monitoring of the aquatic environment (van der Oost et al. 2003). Although no passive sampler is a perfect model for biological organisms and concentration levels obtained from living organisms and passive samplers differ, SPMD samplers are often used to model biomagnification (Yargicoglu and Reddy 2015).

POCIS Application

The demand for the monitoring of polar substances in water in the past resulted in an increased interest among researches worldwide in elucidating the passive sampling processes occurring in POCIS. Latest reviews of Harman et al. and Morin et al. report on the performance of POCIS, in particular the calibration methods used from 1999 to 2012 (Harman et al. 2012; Morin et al. 2012). In the current review, the applications that focus on the passive sampling of pharmaceuticals and personal care products (PPCP) are from the middle of 2011 to 2015 (Table 1). The crucial issues of this sample processing, which is schematically demonstrated in Fig. 3, are discussed and the main features of the traditional POCIS design and the new prototypes are also described. Target analytes and the sampling sites of interests are considered and new findings on the method of calibration are highlighted. Analytical aspects of sample extraction, chemical analysis and biological testing are also included.

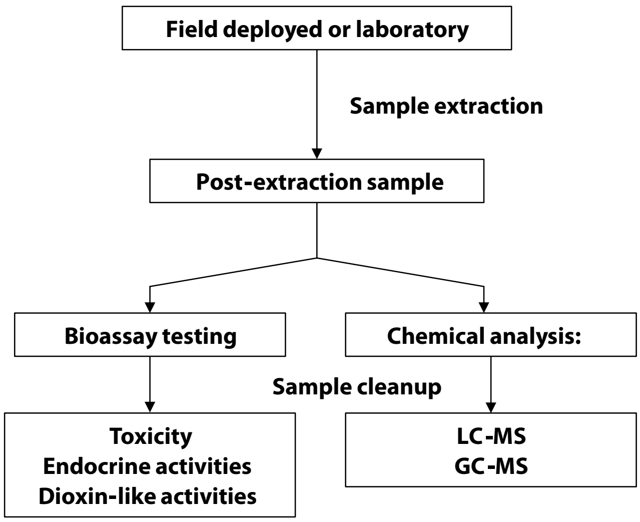

Fig. 3 POCIS processing scheme (modified according to Alvarez et al. 2008).

POCIS Design

The Polar Organic Chemical Integrative Samplers (POCIS) are designed to sample water-soluble organic chemicals from the aqueous environment. As mentioned above, this device relies on diffusion and adsorption to accumulate the analyte. The deployment time usually ranges between weeks and months.

POCIS typically consist of a sorbent, inserted between two microporous membranes that are assembled in a stainless steel housing (Fig. 4). Both sorbent and microporous membrane can vary depending on the particular application. Laboratory-derived calibration data (i.e., data regarding the sampling rate) are only applicable to devices having common surface area-to-sorbent mass ratios, resulting in the necessity of a standardized configuration.

Two different configurations of POCIS are commonly used, each containing a different sorbent. A "Pesticides"

Table 1 Use of polar organic chemical integrative sampler for monitoring of PPCP from the middle of 2011 to 2015.

Aim of the study	Group of targeted analytes	Matrix	Analytical technique	Measured concentrations / maximal exposure duration (days)	Sorbent	Note	Reference
Screening	Antibiotics (vet.)	Agricultural watershed	LC-MS/MS	0.0003–68 ng l^{-1} / 52	HLB	Seasonal occurrence screening	(Jairnes-Correa et al. 2015)
Calibration	NSAIDs	River water WWTP effluent	LC-MS/MS	0.33–0.46 ng l^{-1} / 15	HLB	Stir bar sorptive extraction development Laboratory calibration	(Tanwar et al. 2015)
Screening	NSAIDs, β-blockers, antidepressants, anticonvulsives	WWTP effluent	LC-MS/MS	160–440 ng sampler^{-1}(∑) / 31	HLB	Biological effect on muscle tissue (PAH, PCB)	(Turja et al. 2015)
Screening	Analgesics antidepressants, calcium-channel blockers, benzodiazepines, NSAIDs, β-blockers, anti-histamines, insecticides, antibacte rials/antifungals, stimulants, steroid hormones, chemotherapeutics, cannabinoids	WWTP effluent	UHPLC-MS/MS	0.01 ± 0.01–85.39 ± 4.98 ng l^{-1} / 30	HLB	Grab sampling in parallel Effects on fish	(Zenobio et al. 2015)
Calibration	NSAIDs antibacterials/antifungals	WWTP influents WWTP efluents	LC-UV(FLD)	52.3–127.7 μg l^{-1} 10.7–24.6 μg l^{-1} / 14	HLB	Uptake kinetics Laboratory calibration	(Amdany et al. 2014a)
Calibration	Anticonvulsives, calcium-channel blockers, anti-histamines, antipsychotics, chemotherapeutics, fungicides, anticonvulsives, steroid hormones, hypolipidemics, antibacterials	Lake water estuarine water	LC-MS/MS	0.0012–265 ng l^{-1} / 28	HLB	Tropical ecosystems *In situ* calibration	(Bayen et al. 2014)
Calibration	Wide spectrum of pharmaceuticals	Spiked mineral water	LC-MS	ND	HLB	POCIS-Nylon PRC, laboratory calibration	(Belles et al. 2014)
Forensic	Amphetamines	Sewage (sewer line)	LC-MS/MS	> 3 ng ml^{-1} / 27	HLB	Forensic analysis Proof of concept	(Boles and Wells, 2014)
Screening	69 compounds including PCP	WWTP effluent	GC-MS	5–500 ng l^{-1} / 29	HLB	CLAM and discrete sampler comparison	(Coes et al. 2014)
Screening Bioassay	Steroid hormones, antibiotics, NSAIDs	Pharmaceutical factory area WWTP influent WWTP effluent	LC	Up to μg l^{-1} / 30	HLB	Multireceptor bioassay-based monitoring (hormone, dioxin activity)	(Creusot et al. 2014)
Calibration	NSAIDs	River water Drinking water	LC-MS/MS	0.11–0.67 ng l^{-1} 0.20–0.22 ng l^{-1} / 14	HLB	Recirculating flow system for laboratory calibration	(Di Carro et al. 2014)
Screening Calibration	Analgesics, psycholeptics, antidepressants, illicit drugs	Surface water	LC-MS/MS	463 to 6447 ng sampler^{-1} / 20	Triphasic	Czech aquatic environment *In situ* calibration	(Fedorova et al. 2014)
Screening	Anticonvulsives, chemotherapeutics, hypolipidemics, NSAIDs, antibacterials, artificial sweeteners	Sewage lagoon	LC-MS/MS	0.04 ± 0.01–60.3 ± 8.05 ng l^{-1} / 14	HLB	Seasonal changes in removal SPMD in parallel	(Hoque et al. 2014)
Calibration	Stimulants, anticonvulsives, antibacterials/antifungals, insecticides, diuretics, analgesic	Spiked potable water	LC-MS	LOQ 0.03–0.33 μg l^{-1} / 26	Strata-X	Chemcatchers and grab samples in parallel Laboratory calibration	(Kaserzon et al. 2014)

Screening Bioassay	Wide spectrum of pharmaceuticals	WWTP effluent	LC-MS	ND	HLB Triphasic	Anti-androgenic activity; YAS LDPE and silicone strips in parallel	(Liscio et al. 2014)
Screening Calibration	Anticonvulsives, chemotherapeutics, NSAIDs, hypolipidemics, steroid hormones and sweeteners	Drinking water treatment plants	LC-MS/MS	0.02 ± 0.01–29.83 ± 6.03 ng l^{-1} / 30	HLB	Grab sampling in parallel	(Metcalfe et al. 2014)
Screening	Amphetamines, cocaine and its metabolite, opioids	WWTP proces	LC-MS/MS	40 ± 5–497 ± 9 ng l^{-1} 9 ± 1–497 ± 9 ng l^{-1} / ND	HLB	Removal efficiencies Composite and grab sampling in parallel	(Rodayan et al. 2014)
Screening Calibration	Sulfonamides, Antibiotics, steroid hormones	Estuarine water	UHPLC–MS/MS	Below quantification to 1613 ng l^{-1} / 60	HLB	*In situ* and laboratory calibration Salinity experiment	(Shi et al. 2014)
Screening Calibration	Amphetamines, cocaine and its metabolite, opioids	WWTP	LC–MS/MS	1 ± 0.01–893 ± 208 ng l^{-1} / 14	ND	Removal efficiencies Composite sampling in parallel	(Yargeau et al. 2014)
Screening Calibration Bioassay	Estrogens	Surface water	GC-MS/MS	Mean 1.9 ng l^{-1} (estrone) / 44	HLB	Estrogenity assays YES, T47D-KBluc Assay, E-Screen	(Alvarez et al. 2013)
Stability study	Wide range of pharmaceuticals and PCP	Laboratory samples, river water	UHPLC–MS/MS	6.9 ± 1.3–2130 ± 105 ng sampler^{-1} (storage 255 days)	HLB	Stability on POCIS and SPE cartridges	(Carlson et al. 2013)
Screening Bioassay	Endocrine disrupting chemicals	Surface water	LC	–	HLB	Endocrine and dioxin-like activities (ASE extracts) MELN, MDA-kb2, HG5LN-hPXR, PLHC-1, EROD Sediment/water distribution SPMD in parallel	(Creusot et al. 2013)
Screening Bioassay	Sulfonamides, antibiotics, anticonvulsives, NSAIDs	WWTP in/effluent River water up/downstream	LC-MS/MS	2–18,550 ng sampler^{-1}(Σ) 3–272 ng sampler^{-1}(Σ) / 23	ND	Estrogen-, androgen- and aryl hydrocarbon receptor mediated activities H4IIE-luc, MVLN, MDA-kb2 Cytotoxicity SPMD in parallel	(Jalova et al. 2013)
Screening Calibration	Chemotherapeutics, NSAIDs, β-blockers, corticosteroids	Hospital sewage	UHPLC-MS/MS	0.5 to 12 μg l^{-1} / 7	HLB	Hospital wastewater Laboratory calibration	(Bailly et al. 2013)
Calibration	56 compounds including hormones and pharmaceuticals	Spiked tap water	LC-MS/MS	–	HLB	POCIS-derived accumulation curves Laboratory calibration	(Morin et al. 2013)
Calibration	Alkylphenols (surfactants), steroid hormones	Surface waters WWTP influent WWTP effluent	GC-MS/MS	0.8–66 ng l^{-1} 31–3189 ng l^{-1} 16–62600 ng l^{-1} / 14	Triphasic	PRC Laboratory calibration	(Vallejo et al. 2013)
Screening	Anticonvulsives, antidepressants, NSAIDS, antipyretics, stimulants	Surface waters	LC-MS/MS	1–200 ng l^{-1} / 21	HLB	Trace metals in parallel	(Vystavna et al. 2013)
Screening Calibration	Antibiotics, chemotherapeutics	WWTP	LC-MS/MS	ILOD 0,10–6.96 ng ml^{-1} / 18	o-DGT	Novel passive sampler device 0.5 mm XAD18 agarose binding gel, a 0.8 mm standard agarose diffusive gel	(Chen et al. 2013)
Screening Bioassay	Pharmaceuticals, illicit drugs etc.	Lake water and sediment	LC-MS	1.6–5200 ng l^{-1} / ND	HLB	YES Distribution in depth/sediment SPMD in parallel	(Alvarez et al. 2012)

Screening	Sulfonamides	WWTP up-stream WWTP down-stream	LC-MS/MS	<20–736 ng of sulfamethoxazole equivalents · $POCIS^{-1}$ / 28	HLB Triphasic	Combination with ELISA	(Cernoch et al. 2012)
Screening Calibration	β-blockers, hormones	WWTP in/effluents, WWTP up/downstream	LC-MS/MS	> 249 ng $sampler^{-1}$ atenolol, sotalol 66–113 ng·$sampler^{-1}$ metoprolol, propranolol, bisoprolol < 4 ng $sampler^{-1}$ nadolol, timolol, oxpenolol, betaxolol 355 ng $sampler^{-1}$ estriol / 24	HLB	TWA, PRC *In situ* calibration	(Jacquet et al. 2012)
Screening Bioassay	Antibiotics, chemotherapeutics, antiprotozoal drugs, NSAIDs, anticonvulsives	WWTP up/downstream	LC-MS/MS	3–409 ng $sampler^{-1}$ / 20	HLB Triphasic	Estrogen activities Non-specific cytotoxicity, endocrine-disruptive (ED) potential and dioxin-like toxicity MVLN, H4IIE-luc recombinant *S. cerevisiae*	(Jarosova et al. 2012)
Screening Calibration Bioassay	Antibiotics, amphetamines, opioids, marker of untreated human waste	Surface waters	LC-MS/MS	0.5–71 ng l^{-1} / 30	ND	YES Grab sampling in parallel	(Jones-Lepp et al. 2012)
Screening	Alkylphenols oestrogen hormones, antidepressants, NSAIDs, β-blockers, bronchodilators, hypolipidemics, stimulants	WWTP effluent WWTP up/downstream	LC-MS/MS	ND–1000 ng $sampler^{-1}$ / 28	HLB	Sampling rates, PRC studies *In situ* and laboratory calibration	(Miege et al. 2012)
Screening	Antidepressant, NSAIDs, stimulants, anticonvulsives, bronchodilators, hypolipidemics, alkylphenols	Coastal waters	LC-MS/MS	up to 41 ng l^{-1} / 28	HLB	Mediterranean water	(Munaron et al. 2012)
Screening	Psychiatric drugs, analgesics, broncholidators, NSAIDs, hypolipidemics, stimulants	WWTP up/downstream	LC-MS/MS	Approx. up to 275 ng·l^{-1} / 21	HLB	Socioeconomic study (Ukraine vs. France)	(Vystavna et al. 2012)
Calibration	Analgesic, stimulants, nicotine metabolite, antihistamines steroid hormones	WWTP effluent	LC-MS/MS	0.3 ± 0.2–5.1 ± 1.9 ng l^{-1} / 28	HLB Triphasic	Laboratory calibration 36 compounds with no previously reported R_s values (+ agrichemicals)	(Bartelt-Hunt et al. 2011)
Screening Calibration	Cocaine and its metabolites, amphetamines, morphine, nicotine metabolite, β-blockers' metabolite, antihistamines, anticonvulsives, analgesics, antibiotics, sulfonamides, anthelmintics	Sewage treatment works	UHPLC-MS/MS	5–6389 ng l^{-1} / 14	HLB	Cetirizine back calculation *In situ* calibration	(Harman et al. 2011)
Screening Bioassay	Steroid hormones	Surface water	LC-MS/MS	Not detected / 7	HLB	Endocrine effects hepatic mRNA expression estrogen receptor a (ERa), gonadal expression of P450 aromatase A (caged minnows)	(Jeffries et al. 2011)

Calibration	NSAIDs, antihistamines, steroid hormones, antidepressants, β-blockers, anticonvulsives, chemotherapeutics	Spiked deionized lake and dechlorinated tap water	LC-MS/MS	ND	HLB MAX MCX	Dissolved organic matter, pH effect In house MAX, MCX sorbent Laboratory calibration	(Li et al. 2011)
Screening Bioassay	Antidepressant, steroid hormones alkylphenols, NSAIDs, stimulants, anticonvulsives, hypolipidemics, analgesic, bronchodilators	Surface water	LC-MS/MS	3–20 ng sampler^{-1}(∑) / 30	HLB	Toxicity estrogenic, anti-androgenic and dioxin-like activities MELN, MDA-kb2, PLHC-1	(Tapie et al. 2011)

ND – not defined

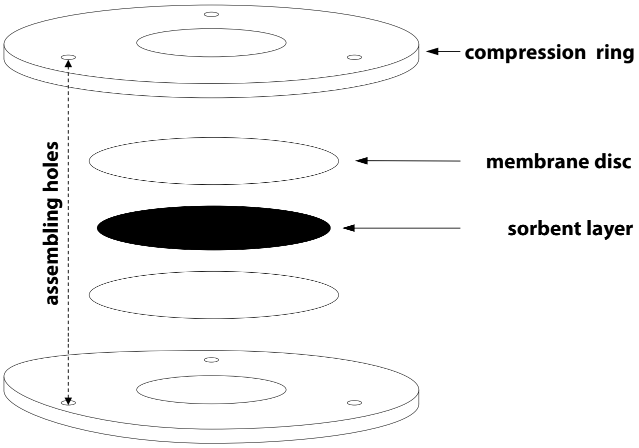

Fig. 4 Structure of the polar organic chemical integrative sampler.

configuration (POCISPest) contains a mixture of three sorbent materials and is aimed at sampling pesticides, natural and synthetic hormones, wastewater-related chemicals and other water-soluble organic chemicals. The sorbent mixture consists of a tri-phasic mixture of a hydroxylated polystyrene-divinylbenzene resin (Isolute ENV+) and a carbonaceous adsorbent (Ambersorb 1500) dispersed in a styrene divinylbenzene copolymer (S-X3 Bio Beads) (Alvarez et al. 2004). A "Pharmaceutical" configuration (POCISPharm) contains a single sorbent, usually Oasis HLB. Oasis HLB is designed for pharmaceutical sampling and is used in most studies of drug contaminants in aqueous environments since most of the classes of pharmaceuticals can be retained by a single sorbent. In comparison, there are limited advantages in using ion exchange sorbents in POCIS (Li et al. 2011). In some cases, both the receiving phases (HLB and triphasic) are deployed together to combine the advantages offered by the different mechanisms and so increase the chance of attracting more analytes (Cernoch et al. 2012; Jarosova et al. 2012; Liscio et al. 2014). Kaserzon et al. 2014 recently used POCIS containing a polymeric reverse phase, the Strata-X™ , to study the kinetics of uptake of several ionizable and polar pesticides, pharmaceuticals and personal care products. Strata-X™ sorbent performed similarly to Chemcatcher™ (SDB-RPS) and are both suitable monitoring tools.

The microporous membrane that covers the sorbent (Fig. 4) serves as a size-selective sieve (typically 0.1 µm pores) that prevents biofouling, but might result in an altered sampling rate. Alvarez et al. (2004) evaluated several commercially available membranes for their use in a hydrophilic integrative sampler. Polyethersulfone (PES) exhibited the best combination: high analyte uptake rates, minimal superficial biofouling and membrane durability, necessary for long-term integrative sampling of polar organic chemicals. PES membrane is also used in both of the commercially available POCIS configurations (Pharm and Pest) and is the most frequently used membrane. Indeed, membranes used in-house assembled samplers are well described in the literature. For instance, there are nylon membranes enabling the sampling of hydrophobic pollutants and with an improved rate of accumulation for other pollutants (Belles et al. 2014). An innovative approach was introduced by Chen et al. (Chen et al. 2012; Chen et al. 2013), which used a gel-based layer instead of a membrane. Such diffusive gradients in thin-films (DGT) samplers were originally used for the measurement of inorganic compounds and were shown to be relatively independent of the rate of water flow (Zhang and Davison 1995). The new configuration initially enabled measurements of organic chemicals (o-DGT) in the laboratory (Chen et al. 2012). This method was later validated and used for the routine monitoring of various antibiotics in wastewater (Chen et al. 2013).

Target Analytes and Sampling Sites

The analytical processes used to assess hydrophobic compounds (Kow > 3) in aquatic environments are quite well characterized and the use of passive samplers (e.g. SPMD, LDPE, silicone rubber) for routine environmental monitoring is already a well-accepted procedure. POCIS can be considered as a complementary method because of the good affinity of this method for compounds with a log Kow < 4 (Alvarez et al. 2004), which includes hydrophilic compounds such as pharmaceuticals, household and industrial products, hormones, herbicides and polar pesticides.

Antibiotics and chemotherapeutics, antidepressants, anticonvulsants, steroid hormones, NSAIDs, antipyretics, antihistamines, β-blockers, illicit drugs, stimulants, insecticides, fragrances, surfactants, alkylphenol compounds are the most frequent classes of pharmaceuticals and personal care products discussed in the literature (Table 1). Indeed, the correlation between exposure to humans/domestic animals and the abundance of these compounds in the water environment is obvious. Screening studies usually cover a wide range of chemicals in order to monitor local contamination and/or its seasonal changes. Vystavna et al. (2012; 2013) even compare the profiles obtained from two different regions with contrasting socio-economic conditions. In some cases, only a specific range of substances is included in the study. For instance, amphetamines were monitored in the sewage from an area suspected of illegal drug activities (Boles and Wells 2014). Another two studies are on the removal of illicit drugs during the treatment of sewage (Rodayan et al. 2014; Yargeau et al. 2014). Alvarez et al. (2013) and Jeffries et al. (2011) address the analysis of steroid hormones in their studies, whereas Cernoch et al. (2012) analyse only sulfonamides. A number of POCIS studies are also coupled to bioassays, evaluating endocrine-disruptive potential or dioxine-like activities (Jeffries et al. 2011; Tapie et al. 2011; Alvarez et al. 2012; Jarosova et al. 2012; Alvarez et al. 2013; Jalova et al. 2013; Creusot et al. 2014).

The inputs and outflows from wastewater treatment plants (WWTP) and the river upstream and downstream close to a WWTP, respectively, are common POCIS sampling sites. In some cases, specific regions are studied such as tropical waters (Bayen et al. 2014), Mediterranean coastal waters (Munaron et al. 2012) or estuarine waters (Bayen et al. 2014; Shi et al. 2014). POCIS are also deployed in agricultural watersheds (Jairnes-Correa et al. 2015), areas of pharmaceutical industrial activity or hospital effluents (Bailly et al. 2013), to investigate the degree of contamination by particular pollutants. Spiked water samples and laboratory tests are commonly used in studies on the kinetics of uptake of new micropollutants and evaluation of various physical effects on the sampler or the characterization of the innovative features of future POCIS (Li et al. 2011; Carlson et al. 2013; Morin et al. 2013; Belles et al. 2014; Kaserzon et al. 2014). These approaches often include a range of analytes with different physical-chemical properties (basic, acidic, phenolic and neutral) which provide a better insight into the new samplers' efficiency for monitoring various analytes.

Calibration, Sampling Rates and Performance of a Reference Standard (PRC)

It is difficult to obtain reliable information on the kinetics of uptake of polar compounds and the effects of environmental factors (e.g. temperature, turbulence and biofouling). Determination of sampling rate is not straightforward as it takes a lot of time to obtain reliable sampling rate values (R_S). A standard calibration procedure is still lacking and different approaches often involve the use of original laboratory devices, which results in variability in the determined R_S values. Even though it is also virtually impossible to consider all the factors operating in the field, laboratory calibration is still the most popular method for evaluating R_S (Bartelt-Hunt et al. 2011; Li et al. 2011; Miege et al. 2012; Morin et al. 2013; Vallejo et al. 2013; Amdany et al. 2014a; Bayen et al. 2014; Belles et al. 2014; Di Carro et al. 2014; Kaserzon et al. 2014). *In situ* calibration, at specific sites is more reliable but so far has rarely been used (Harman et al. 2011; Jacquet et al. 2012; Miege et al. 2012; Shi et al. 2014) because of the complexity of the process. Shi et al. (2014) compare both field and laboratory sampling rates for assessing ATB and endocrine disruptive compounds in estuarine waters. In this case, the field sampling rates were significantly higher for most of the compounds studied. Miege et al. (2012) compare *in situ*, laboratory and existing literature values. The differences in R_S values are ascribed to differences in the POCIS, temperature, turbulence or exposed surface area. These authors also report that the R_S values (*in situ* calibration) tend to be lower in WWTP effluents, which are characterized by a higher conductivity, higher concentrations of particulate suspended matter and dissolved organic carbon. It should be noted, however, that some screening studies use previously reported R_S values. To date, comprehensive reviews (Harman et al. 2012; Morin et al. 2012) of the R_S values of polar compounds provide supporting material. The use of a performance reference standard (PRC), which can eliminate the influence of environmental factors (already established for hydrophobic samplers), is still limited for hydrophilic compounds. Since Mazzella et al. (2010) proposed deuterated deisopropyl-atrazine-d5 (DIA d5) as an appropriate PRC for polar herbicide sampling, other compounds have been tested (Jacquet et al. 2012; Miege et al. 2012; Vallejo et al. 2013; Belles et al. 2014). Several deuterated hormones and β-blockers are also suggested by Jacquet et al. 2012. Of a variety of hormone and β-blockers tested by Miege et al. (2012) only deuterated atenonol appeared to be a good potential PRC. Two other deuterated compounds ([$^2H_3$]-E2 and [$^2H_4$]-EQ) were successfully used by Vallejo et al. (2013).

Extraction and Analytical Techniques

Extraction of the analyte from a receiving phase after in-field exposure is the next step in the sample processing and the method may vary depending on the sorbent used and the character of the analyte. Methanol (MeOH) is usually used for the extraction when POCISPharm is used. Other extraction media, e.g. ACN (Amdany et al. 2014a), acetone (Tanwar et al. 2015), MeOH/water (Bailly et al. 2013; Creusot et al. 2014) or MeOH/dichloromethane (Vystavna et al. 2012; Creusot et al. 2013;

Morin et al. 2013; Vystavna et al. 2013) are also suitable. Some authors adjust the pH in order to improve the extraction (Harman et al. 2011; Cernoch et al. 2012; Bayen et al. 2014; Shi et al. 2014). Fixed ratio of solvents (dichloromethane: MeOH: toluene, 8:1:1) is common for POCISPest sorbent extraction. Kaserzon et al. (2014) describe a procedure for extraction of Strata-X™ sorbent using MeOH, acetonitrile and acetone. POCIS containing MCX and MAX sorbents can be eluted using MeOH with an addition of 5% ammonium hydroxide and 2% formic acid, respectively (Li et al. 2011). A study dealing with the stability of pharmaceuticals and other polar organic compounds stored in POCIS and solid phase cartridges indicates they remain relatively stable and suitable for ex-post analysis for 20 months when stored at −20 °C (Carlson et al. 2013).

Liquid chromatography is the method of choice in the majority of the studies surveyed and gas chromatography in cases dealing with steroid hormones or alkylphenols because of their low solubility in water (Alvarez et al. 2013; Vallejo et al. 2013; Coes et al. 2014). Tandem mass spectrometry is almost always mandatory since the detection of trace amounts of pollutant is required. With these analytical approaches, concentrations of PPCPs in the field can be reliably determined within the range of ng l^{-1} or ng $sampler^{-1}$ (Table 1). LC with UV and fluorescence detection (FLD) was used by Amdany et al. (2014a), whereas Cernoch et al. successfully used a POCIS in combination with an immunochemical ELISA technique for a semi-quantitative screening of sulfonamides, which gave similar results to the LC-MS (Cernoch et al. 2012).

Bioassays

The extracts from POCIS can be further used to assess the biological effects of water contaminants. A yeast estrogen screen (YES) is commonly used to evaluate estrogen in the environment (Alvarez et al. 2012; Jones-Lepp et al. 2012; Alvarez et al. 2013), but is not suitable for accurately assessing estrogenic activity at lower concentrations (Alvarez et al. 2013). In comparison, E-Screen and T47D-KBluc bioassays are more sensitive. Multi-receptor *in vitro* bioassays are often used to determine overall non-specific cytotoxicity, endocrine-disruptive potential and dioxin-like toxicity (Jeffries et al. 2011; Tapie et al. 2011; Jarosova et al. 2012; Jalova et al. 2013; Creusot et al. 2014). Recombinant *S. cerevisiae* or MELN, MDA-kb2 and H4IIE-luc cell lines are the most commonly used. The extracts from SPMD (Alvarez et al. 2012; Jalova et al. 2013), LDPE, silicone strips (Liscio et al. 2014) or sediment samples subject to accelerated solvent extraction (Creusot et al. 2013) should also be measured in parallel in order to complete and compare the results of the biological testing of the POCIS extract, since they could contain different classes of compounds. For instance, the arylhydrocarbon-mediated potency in both SPMD and POCIS indicate that both hydrophobic and polar compounds contribute to the overall dioxin-like potential of samples (Jalova et al. 2013). These authors also report that the cytotoxicity of wastewater is not correlated with the estrogenic or androgenic potencies, which are primarily caused by steroidal estrogens. The cytotoxicity of the POCIS extracts in the yeast assay is associated with antibiotics and other pharmaceuticals (Jalova et al. 2013).

Conclusions

Despite its relatively long history, passive sampling is an innovative monitoring tool, particularly in the context of monitoring environmental pollutants. The main benefits of passive sampling are the simplification of the overall sampling procedure, reductions in cost and solvent use and miniaturization. In addition, there are many factors that need to be considered when passive sampling is used in monitoring programs. Probably, the most important of these are the environmental conditions (flow, biofouling, temperature), which can strongly affect the accumulation of the target analyte in the sampler. Thus, in order to accurately determine the sampling rates for a wide range of new contaminants further detailed research is needed.

Passive sampling of pharmaceuticals in aquatic environments is most often used for the determination of time-weighted average concentrations or environmental screening. Though the concentrations differ for individual pharmaceutical and personal care products, the concentration usually remains within the range of ng up to μg per litter.

It would be of great value to use POCIS samplers for assessing and managing groundwater pollution. Moreover, the improvement of existing procedures and the search for new methods of passive sampling could, in the future, lead to the inclusion of additional substances into the monitoring programs and a lowering of the limits of detection.

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CHARACTERIZATION OF CARBOFURAN BOUND RESIDUES AND THE EFFECT OF AGEING ON THEIR DISTRIBUTION AND BIOAVAILABILITY IN THE SOIL OF A SUGAR BEET FIELD IN NORTH-WESTERN MOROCCO

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ABSTRACT

This study was undertaken to investigate distribution, fractionation, bioavailability and remobilization characteristics of bound soil-aged carbofuran and the effect of ageing in clay soil in a typical field of sugar beet at Loukkos in northwest Morocco. Results indicate that initially there were high levels of bound residues (BR) in the humin fraction, which decreased with incubation time and ageing of the BR. While in the fulvic and humic acid fractions, the amount of BR increased with the ageing of the BR and occurred predominantly (60%) in the fulvic acid fraction. The possibility of the mineralization and release of BR with ageing was studied using fresh soil and an incubation period of 90 days. The results indicate that the ageing of the residues have a great influence on the remobilization and mineralization rates of carbofuran BR; 9.45 to 14.90% of the total BR was released as extractable residues, and 1.95 to 4.15% was mineralized depending on the age of the residues in soil and the soil-aged carbofuran BR. The incorporation of the residues in the humin fraction is considered to be a threat to the environment. On the other hand, the clear prevalence of residues in the fulvic and humic acid fractions, may have an important effect on their bioavailability and movement in soil. Moreover, the re-extractability of BR could pose a potential environmental risk. Consequently, the BR remobilized must be taken into account when assessing for registration processes the environmental risk of pesticides persisting in soils.

Keywords: aging, carbofuran, bound residues, ^{14}C-technique, extractability, soil organic matter fractionation

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Introduction

Previous investigations show that pesticides bind almost irreversibly with soil constituents, including organic compounds, resulting in the formation of non-extractable bound residues (Führ 1987; Calderbank 1989; Khan and Behki 1990; Gevao 2000; Nowak et al. 2011; Liu et al. 2013; Kästner et al. 2014). These chemical entities are defined as pesticide residues that are not extractable using current methods. They are not extractable using methods that do not significantly change their nature (Roberts et al. 1984; Fuhr et al. 1998).

Because of the difficulty of extracting these residues using conventional analytical methods total pesticide residues tend to be underestimated (Führ 1982; Khan 1982; Calderbank 1989). The use of molecules radiolabelled with ^{14}C has revealed that pesticides remain firmly bound to the soil matrix. This is the result of changes in the stabilization process of the sorption phenomena from weak to strong adsorption sites and diffusion and sequestration or entrapment by sites, during which pesticides and their degradation products become increasingly more stable and less available (Bertin and Schiavon 1989; Senesi 1992; Loiseau 2001; Barriuso and Benoît 2006).

As summarized in Gevao et al. (2003), these residues become increasingly unavailable to the biota, less toxic and less likely to desorb from humic substances over time. For the environment this reduction in bioavailability and accessibility is beneficial. However, there might be processes, which cause an irreversible release of sorbed residues over time (Khan and Ivarson 1981, 1982; Yee et al. 1985; Barriuso et al. 2004). The extent of the reversibility between unavailable and available forms of bound residues (BR) is likely to play an important role in the long-term fate of pesticides (bioavailability) (Barriuso et al. 2008).

Two main mechanisms are involved in BR formation: (i) Covalent(s) binding between pesticides or their degradation products and soil constituents; (ii) physical entrapment of the compound or its degradation products in soil matrices (Bertin and Schiavon 1989; Calderbank 1989; Bollag et al. 2002). Regardless of the mechanism, soil organic matter is involved in their formation.

The extent of the formation of BRs varies depending on the compound, but it may result in a significant part of the residues remaining in the soil, ranging, in general, from 7 to 95% of the dose initially applied (Bollag and Loll 1983; Führ 1987; Calderbank 1989).

Bioavailability of Bound Residues

Bound pesticide residues may give rise to a number of concerns. Among these are questions of bioavailability, runoff, leaching into natural waters and potential long-term effects on soil quality.

Benicha, M., Mrabet, R., Azmani, A.: Characterization of carbofuran bound residues and the effect of ageing on their distribution and bioavailability in the soil of a sugar beet field in north-western Morocco
European Journal of Environmental Sciences, Vol. 6, No. 1, pp. 57–63

On the other hand, BR formation can be regarded as a stabilization process leading to an increase in the persistence of pesticides in soils. However, the formation of BRs pose problems concerning their fate and potential long term risks (Kacew et al. 1996; Alexander 2000). From an environmental point of view, it appears that their immobilization is advantageous and may be regarded as a process contributing to reducing the risk of these residues polluting soil and water (Calderbank 1989; Barriuso and Benoit 2006; Barriuso et al. 2008). Because of their possible release/remobilization by a variety of processes (Gevao et al. 2005) these residues can become potentially bioavailable in the future and may then constitute a threat to soil quality (Burauel and Führ 2000) and sensitive crops (Novak et al. 1995; Scheunert and Reuter 2000; Gevao et al. 2001; Han et al. 2009) and subsequently contribute to diffuse pollution (Dec et al. 1990; Barriuso et al. 2008) and contaminate drain and groundwater resources (Khan 1982; Capriel et al. 1985).

For the environmental risk assessment, it is essential to determine whether the bound residues are permanently retained or gradually released into the soil solution and therefore become again bioavailable for plants, living organisms and are likely to contaminate water resources. On the other hand, study of the localization of sites of BRs in soil organic fractions is of great interest as long as it is used to estimate the risk of residues being mobilized. It has been the subject of a number of studies (Nichiolls 1988; Bertin and Schiavon 1989). Khan and Hamilton (1980) demonstrate that bound residues are located in 3 major fractions of soil organic matter, i.e. fulvic acid (FA), humic acid (HA) and humin (H).

Carbofuran 2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) is among the most widely used carbamate insecticide and nematicide worldwide due to its broad spectrum of effectiveness against a wide range of insects and pests on several crops, including wheat, sugar beet, sugar cane, corn, rice, potato, cotton, sunflower, etc. (Chapalamadugu and Chaudhry 1992; Jaramillo et al. 2000; Ezzahiri et al. 2015). As a result, it has attracted more attention as an alternative to the more persistent and highly toxic organochlorine insecticides (Goad et al. 2004; Saxena et al. 2013).

However, despite its efficacy as an agricultural pesticide, Furadan® has been restricted or banned in many countries, including the USA and Canada (Erwin 1991; Agriculture Canada 1993). However, in Morocco, as in many countries (Gnanavelrajah and Kandasamy 2012; Otieno and Schramm 2012; Khairatul et al. 2013), it is still used in large amounts, particularly in sugar beet and tomato crops, against many insects, root worms and earthworms (Ezzahiri et al. 2015).

Experiments on the long-term fate of ^{14}C-labeled pesticides in soils are rarely conducted. There are no studies on the effect of old carbofuran bound residues on remobilization and mineralization of long term–aged ^{14}C-labelled pesticide residues, which are necessary for a better understanding of the remobilization of carbofuran bound residues under changing abiotic conditions. Therefore, the present study investigated the distribution of carbofuran BR in soil, their biodegradation and the influence of ageing on their fate in soil in at Loukkos, an important agricultural area in north western Morocco, characterized by intensive agriculture mainly consisting of horticultural cultures, sugar beet, sugar cane, etc. According to the national statistics the area under sugar beet (65,000 ha) (Doukkali et al. 2009) is annually sprayed with about 1300 tons of this insecticide, with more than 100 tons applied at Loukkos (5140 ha). With increase in population and increase sugar consumption, currently estimated at 34 kg/person/year (Bouziane 2011), efforts are being made to intensify sugar beet production to attain national self-sufficiency in sugar production, which is among the recommendations of the Green Moroccan Plan, a new government agricultural development strategy (ADA 2009). On the other hand, although frequently invoked to explain the decreases in pesticide degradation with time (e.g. Boivin et al. 2004; Amellal et al. 2006; Kästner et al. 2014), the relationship between the ageing of the bound residues of pesticides and their biodegradability by re-incubation of differently aged BR in fresh soil has been poorly investigated (Lerch et al. 2009).

Understanding the behaviour of bound residues of carbofuran in the environment, is essential for determining the long-term fate and significance of this potential reservoir of contaminants and to develop strategies for remediation and prevention of adverse effects on the environment caused by using it to treat fields of sugar beet.

The specific objectives of this work were (i) to study the distribution of bound residues of ^{14}C-carbofuran in different organic matter fractions of soil, (ii) to evaluate the potential mineralization of carbofuran bound residues in soil, (iii) to estimate their risk of being remobilized as a result of ageing, and finally (iv) to quantify the effect of ageing on the distribution of carbofuran BR in the different organic matter fractions in soil and their bioavailability in soil, in order to improve risk assessment.

Materials and Methods

Soil Samples

The soil samples used in this study were obtained from a previous study on the dissipation of ^{14}C-carbofuran over a period of 168 days using soil columns (Benicha and Azmani 2005). We used different aged soil samples (from 7 to 168 day samples: the compound had aged for 7 to 168 days in soil) which contained ^{14}C-carbofuran BR residues. The BR soil samples were used after complete soxhlet extraction using methanol, air drying, crushing and homogenizing. Samples of fresh soil were also collected from around the perimeter of Loukkos. Its physical and chemical characteristics are presented in Table 1.

Table 1 Physical and chemical characteristics of the soil used.

pH (water)	pH (KCl)	Total N (%)	Organic Matter (%)	Clay (%) (<2 mm)	Silt (%) (2–50 mm)	Sand (%) (50–200 mm)	CEC (meq/100)
7.8	7.3	0.2	2.1	50.2	35.6	14.2	43.4

Distribution of Bound Residues in Different Organic Matter Fractions in the Soil

To localize ^{14}C-carbofuran BR in soil, we fractionated organic matter using Thibaud et al. (1983) method. The soil was mixed with 0.1N NaOH and 0.1M sodium pyrophosphate ($Na_4P_2O_7$) solutions and shaken for 1 hour. The mixture was then centrifuged at 4000 rpm for 20 min. The precipitate obtained is the humin (H) fraction. Alkaline extracts contain humic (HA) and fulvic (FA) acids. HA was precipitated by adjusting the pH solution to 2 with H_2SO_4. After 30 min at 4 °C, solutions were centrifuged at 4000 rpm for 20 min and the supernatant containing FA was recovered. Precipitated HA were dissolved in 10 ml of 0.1N NaOH and the radioactivity of HA and FA was measured using a Liquid Scintillation Counter (LSC). HA fraction was quantified using a Biological Material Oxidizer (BMO) and the $^{14}CO_2$ formed was quantified (LSC).

Mineralization and Bio-Release of Carbofuran Bound Residues

Extracted soil sample (50 g) was mixed with 50 g of the same type of soil (freshly collected and sieved to 2 mm) and placed in standard biometric flasks at room temperature. 20 ml ethanolamine (scintillation grade) was placed in the side arm of the flasks to trap the $^{14}CO_2$ released. Distilled water was added to the mixture in order to maintain humidity equivalent to 60% of water holding capacity. The flasks were then closed and the humidity controlled and adjusted periodically by weighing the flasks. The experiment was carried out over a period of 90 days. The samples were collected, in triplicate, after 0, 30, 60 and 90 days of incubation. The $^{14}CO_2$ released was quantified (LSC) and the soil in each sample was soxhlet extracted in methanol to determine the quantity of residue rendered extractable. The new extracted soil samples were then air-dried and combusted, using BMO to determine amount of residue still bound to the soil.

Determination of Bound and Total Residues

The determination of total and bound residues was carried out using a Biological Material Oxidizer (Harvey OX600). The $^{14}CO_2$ obtained after combustion of a soil sample (10 g) at high temperatures (900 °C) for 5 min, was trapped in scintillation grade ethanolamine (10 ml) and the radioactivity determined by measuring 1 ml of the solution in the liquid scintillation counter.

Determination of Extractable Residues

50 g (dry weight basis) soil samples were extracted in a soxhlet extraction apparatus with methanol for 4 h (5–6 cycles/h). The procedure was continued until the extracts were no longer radioactive. Methanol was concentrated to 10 ml in a Rotavapor, Buchï, Switzerland at 30 °C and then 1 ml methanol extract was mixed with toluene based scintillator and radio assayed.

Radioactivity Measurement

Radioactivity was measured using a liquid scintillation counter Packard Tricarb 1100 after a cocktail xylene-based solution containing PPO (2,5-diphenyl oxazole), POPOP (1.4-bis/2-(5-phenyloxazolyl)benzene) and naphthalene was added to the sample. The internal standard was used to correct for any quenching effect.

Results and Discussion

Distribution of Carbofuran Bound Residues in Soil Organic Matter

The distribution of carbofuran bound residues in the different organic fractions in soil determines their bioavailability and fate. The fractionation of the organic matter revealed that bound residues were present in all the fractions. The result showed that initially the bound residues were mainly in the humin fraction with more than 50% of the BRs. With ageing, however, these residues were released from the humin fraction and incorporated into humic fractions, i.e. FA and HA, with most in the FA fraction (Fig. 1). Thus, after 168-days of incubation (aged sample) large amounts of these bound residues were incorporated in the FA fraction with 42.03% as against 28.96% and 29.01%, respectively, for the H and HA fractions, whereas after 7 days of incubation, FA contained only 26.43% as against 22.94% and 50.63%, respectively, for the HA and H fractions.

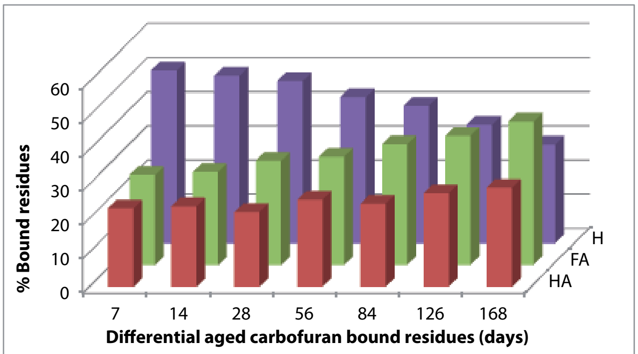

Fig. 1 The percentage distribution of different aged carbofuran bound residues in the different organic matter fractions in soil (FA: fulvic acid, HA: humic acid, H: humin).

Similar results are reported in the literature. After 20 days of incubation of carbofuran in a clay-loam soil, the FA fraction contains 44% of the bound residues, followed by HA with 38% and humin with 20% (Hussain et al. 1986). Lee and Park (1995) report that the non-extractable carbofuran residues are mainly located in soil organic matter in the order FA > H > HA. Carbofuran non-extractable bound residues in the humin soil organic fraction ranged from 52 to 55%, with FA containing from 32 to 39% and HA from 9 to 11% of the total BR (Lee et al. 1987).

Prevalence of BR in the FA fraction is also reported for other pesticides. Khan and Hamilton (1980) found that the residues of prometryn in the H fraction move over time into the FA and HA fractions. On the other hand, Barriuso et al. (1991) report that Atrazine residues are first bound to FA and finally to humin.

The high accumulation of residues in water-soluble fulvic and humic acids (74.04%) has important environmental consequences since it is not only available to plants, but also for soil and aquatic organisms. Lewandowska (2004) report that residues of 2,4-D bound in the soil are available for wheat plants. Most radioactive residues detected in the soil are in the water-soluble FA fraction. Therefore, these residues are available not only for plants, but also for soil and aquatic organisms. Khan (1982), Capriel et al. (1985), Bertin and Scaviona (1989) and Andreux et al. (1991), who chemically fractioned the soil organic matter, report that the FA content of soil plays an important part in the initial rapid immobilization of pesticides. This is also reported by Andreou et al. (2009) who records a great association with and enrichment of the FA fraction of the organic carbon in soil determining the distribution of BR of isoproturon, diazinon and cypermethrin pesticides. Khan (1982) and Lewandowska and Weymann (2002) consider that these residues of atrazine as potentially available for plants, soil and water fauna.

The abundance of carbofuran bound residues in FA is probably related to interactions with the polar groups that abundantly occur in the FA fraction, as suggested by Loiseau et al. (2002) for atrazine bound residues.

Bioavailability of Carbofuran Bound Residues

The bioavailability of carbofuran bound residues is presented in Fig. 2. This shows that the re-extractable residues ranged from 9.45 to 15% of the total amount, while 1.95 to 4.15% of the total bound residues were mineralized ($^{14}CO_2$ release) depending on the incubation time and ageing of BR in the soil.

The results indicate a significant increase in BR extractability with incubation time. For the 7-day sample, 9.45% of the residues were extractable and after three months it was 14.90% (Fig. 2). The same tendency was recorded for the mineralization rate. For the same 7-day sample, 1.95% were mineralized after one month and increased to 4.15% after three months of incubation.

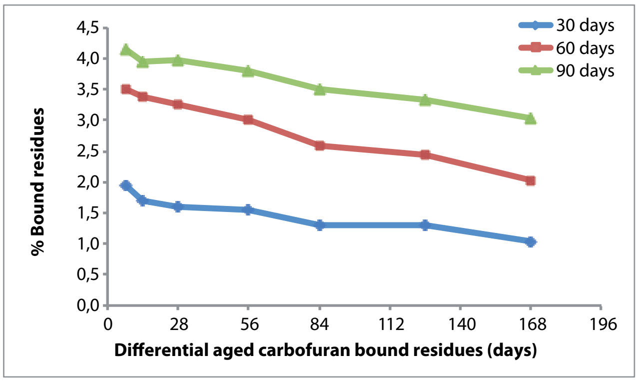

Fig. 2 Release of different aged ^{14}C-carbofuran bound residues with incubation time (Re-extractability of carbofuran bound residues).

On the other hand, there was a reduction in the carbofuran BR that could be extracted from soil samples with ageing. Extractability of the carbofuran BR decreased with ageing, to 10.6% for the 168-day sample compared to 14.9% for the 7-day sample. However, the longer the BR is incubated with fresh soil the greater the increase in the extractability of BR (from 1 month to 3 months). At the end of the third month of ageing, methanol soxhlet extracts of the 7-day sample were 9.45%, 11.35% and 14.90% of the aged carbofuran BR, for 1, 2 and 3 months respectively, while it was only 6.39%, 8.80% and 10.60% for the 168-day sample for the same periods.

This gradual decrease in the release of BR with ageing is probably due to the fact that BR formed immediately after the application of carbofuran (7 and 14 days samples) are released more quickly than those that form after a long term interaction with the soil. The same tendency was recorded for the mineralization rate of BRs; a gradual decrease with age. This gradual decrease with age of both re-extractable and mineralized quantities, could be due to the fact that the BRs become more stable the longer they are in the soil. These findings support the results on the sorption of carbofuran by soil (Benicha and Azmani 2005); their break down becomes increasingly difficult with time due to the interactions with soil components, with which the molecule becomes progressively more tightly bound, or entrapped in, the organic matrix and correspondingly more stable and less bioavailable (Ahmad et al. 2004; Barraclough et al. 2005) (ageing process).

Andrea and De Wiendl (1995) report the same for lindane with the formation and bio-release of lindane BR varying depending on soil type and ageing of the compound in the soil. Johnson et al. (1999) show that a significant reduction in atrazine BR extractability occurs with ageing. They report that extractability of BR decreases from 96% after 1 week to 66% after 3 months of ageing. Nakagawa et al. (2000) report a small release of up to 3.5% of ^{14}C-atrazine BR from soil following the addition of an inoculum of microorganisms. Nam and Kim (2002) report a decline in the bioavailability of PAH with increase in residence time.

BR Mineralization rates were low and did not exceed 4.15% and declined with age (from 7 to 168-days). Their re-extractability rates however, were significantly higher, up to 15% after 90 days incubation (7-day sample). This suggests that microorganisms initially release the BR by breaking down bonds between molecules of the insecticide and the soil matrix, then degrade and mineralize them for use as a nutrient source (Ladd 1989; Khan and Behki 1990; Hayar 1997).

Results of Khan and Behki (1990) show that 30-35% of BR of atrazine can be extracted from soil inoculated with fresh soil after 83 days. Gevao et al. (2001) also report that the re-extractability of atrazine BR is of the same order (24% of BR). Khan and Ivarson (1981) report a release of 27% of the BR of prometryn by soil microorganisms after 22 days of incubation of soil containing BR associated with fresh soil. They report, however, that the evolution of $^{14}CO_2$ during this period was negligible. For the same pesticide incubated in another type of soil Khan and Ivarson (1982) report the release of 25–30% of BR after 28 days of incubation with fresh soil. They report a low mineralization rate, which indicates that the breakdown of the aromatic ring of the product is a minor reaction. Roberts and Standen (1981) show that 25–40% of cypermethrin residues are mineralized after incubation of soil BR with fresh soil. Nakagawa et al. (2000) report that ^{14}C-atrazine BR is released from soil after the addition of an inoculum of microorganisms but very little $^{14}CO_2$ was produced: less than 0.8%.

Our results also show that mineralization rates decrease with ageing of carbofuran BR. This could be explained by the fact that old BRs are very tightly bound to soil and very stable. These results confirm those obtained by others in that ageing reduces the mineralization of pesticides (Chung and Alexander 1998; Regitano et al. 2006). Hatzinger and Alexander (1995) report that mineralization of phenanthrene and 4-nitrophenol in soils decreases with ageing, which also increases the resistance of phenanthrene to biodegradation and extraction. Alexander (2000) report that laboratory tests confirm the lower availability to microorganisms of aged than of unaged compounds in different soils. The bioavailability to microorganisms decreases with time. Field ageing also diminishes the availability to microorganisms of many pesticides (Scribner et al. 1992; Weissenfels et al. 1992). Nam and Kim (2002) report that mineralization rates of phenanthrene aged in the humin-mineral fraction significantly decreased with time.

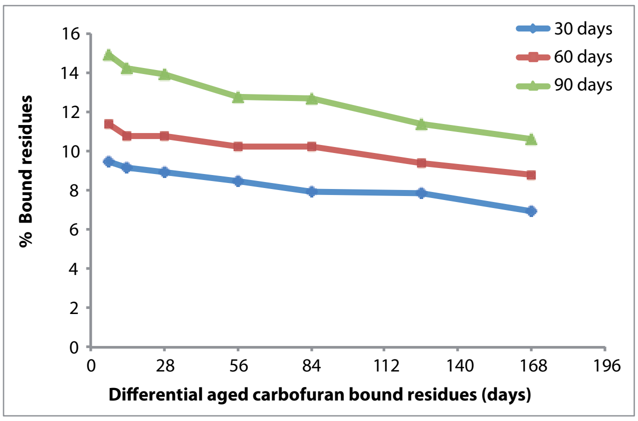

Fig. 3 Mineralization of different aged ^{14}C-carbofuran bound residues with incubation time (Emission of $^{14}CO_2$).

Conclusions

This study investigated the fate of carbofuran BR and the influence of ageing on the extent to which they are bound into organic matter fractions and their bioavailability. The distribution experiment revealed the presence of substantial amounts of carbofuran BR in water-soluble soil fractions (FA and HA). As a result, residues in this fraction are more bioavailable and thus their movement in soil constitute an environmental risk. On the other hand, their bioavailability (possibility of remobilization) increases when fresh soil is added, with re-extractability up to 15% and a mineralization rate of 4.15% over 90 days. This release of part of the residues can be a source of environmental pollution. The results also show that ageing has an effect on mineralization and extractability of carbofuran BR; the older the BR, the more difficult their release and mineralization. This is important information for environmental management and environmental risk assessment of pesticides. Therefore, the formation of bound pesticide residues in soil should be taken into account when assessing risk of applying chemicals to soils.

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THIENEMANNIA SPIESI SP. NOV., A CRENOPHILOUS SPECIES FROM THE SCHAPBACH QUELLE, BAVARIA, GERMANY (DIPTERA: CHIRONOMIDAE: ORTHOCLADIINAE)

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ABSTRACT

A description of the male and female imago and pupal exuviae of *Thienemannia spiesi* sp. nov. is provided based on material collected in the Schapbach Quelle (spring), Bavaria, Germany. This description increases the total number of species known worldwide in the genus to eleven. The new species, *T. spiesi*, can be distinguished from other related species (except *T. libanica* Laville and Moubayed 1985) by the following combination of characters: chaetotaxy of the wing membrane, inferior volsella nose-shaped and not sinuous, gonostylus bearing a crista dorsalis, spines present on tergite VII of the pupal exuviae. Comments on its ecology and taxonomic position are provided.

Keywords: Diptera, Chironomidae, *Thienemannia spiesi* sp. nov., ecology, distribution

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Introduction

The present description is based on adults, pharate adults and pupal exuviae belonging to two species of the genus *Thienemannia* Kieffer, 1909. Specimens examined belong to *T. libanica* Laville and Moubayed, 1985 (from Lebanon) and *T. spiesi* sp. nov. (from Germany) and both are closely related and considered to be sister species based on both adults and pupal exuviae. In Moubayed-Breil and Ashe (2013) *T. spiesi* sp. nov. is listed under the name *Thienemannia* sp. 1. The pupal exuviae of the new species resembles those of two recently described species: *T. corsicana* Moubayed-Breil 2013 (Moubayed-Breil 2013) and *T. valespira* Moubayed-Breil and Ashe 2013 (Moubayed-Breil and Ashe 2013). Records of *T. libanica* listed in Schacht (2010) and Sæther and Spies (2013) from Germany are referable to *T. spiesi* sp. nov. and those from elsewhere in Europe (Denmark, France, Luxembourg, Portugal, Spain) are probably misidentifications of either *T. spiesi* sp. nov. or some other related species. With the description here of *T. spiesi* sp. nov., there are now eleven valid species of *Thienemannia* Kieffer, 1909 known worldwide. The genus *Thienemannia* is known from the western Palaearctic (Europe and the Near East), the Nearctic and the Oriental Region (Ashe and O'Connor 2012).

The description of the male and female adult and pupal exuviae of *T. spiesi* sp. nov. is given based on material collected in Schapbach Quelle (30.VII.1999, altitude 1,170 m, Bavaria, Germany) which had previously been misidentified as *T. libanica*. Terminology and measurements follow Sæther (1980, 1985) and Langton and Pinder (2007) for the male adult and Sæther (1980) and Langton (1991) for pupal exuviae. Comments on the taxonomic position and ecology of the new species are given.

Thienemannia spiesi sp. nov.

Thienemannia libanica: in Schacht (2010), misidentified.

Thienemannia sp. 1: in Moubayed-Breil and Ashe 2013 (Figs. 19–20, 32)

Material Examined

Holotype: GERMANY: Bavaria, Nationalpark Berchtesgaden (BGL), Schapbach Quelle (spring), altitude 1,170 m, 30.VII.1999, 1 pharate adult male.

Paratypes: 4 pharate adults (2 males and 2 females) including 4 associated pupal exuviae (2 males and 2 females); same locality and date as holotype.

Holotype and paratypes are deposited in the collection of the Zoologische Staatssammlung (ZSM), Munich, Germany. Type material was mounted on five slides in polyvinyl lactophenol mountant.

Etymology: The new species is named *spiesi* after our colleague Martin Spies from the Zoologische Staatssammlung (ZSM), Munich, Germany, in appreciation for his assistance and the loan of material.

Description

Male imago (Figs. 1a, 1e, 1f, 1h; 2a–d)

(n = 3 pharate adult males)

A relatively small sized species (among the smallest in *Thienemannia*). Total length 1.35–1.45 mm. Wing length 1.15–1.20 mm. General colouration: contrasting dark brown to brown, especially on the thorax. Head and antenna brown including antennal and wing sheath, halteres brown. Thorax dark brown to brown, with brown mesonotal strips. Wing membrane transparent, without shading. Legs dark brown to brown; tarsi of PI, PII and PIII blackish apically.

Head: Eyes hairy between ommatidia, hairs present along proximal half of inner eye margin (Fig. 1a). Temporal setae 2–3, including 2–3 inner verticals, 0 outer verticals, postorbitals absent. Clypeus with 14–16 setae. Palp 5-segmented, length (μm) of segments: 14–16, 19–21, 34–35, 51–55, 73–75; sensilla clavata absent on third segment; last segment bearing 3 apical setae. Antenna 330–340 μm long, 10-segmented (Fig. 1f), segments 1 to 3 globulous (respectively 32, 27, 29 μm long); segments 4 to 8 subequal (each 29–30 μm long); segment 9, 25 μm long; ultimate flagellomere (Fig. 1e) 80–87 μm long, slightly clubbed, bearing 1 long apical seta (30 μm long), sensilla chaetica present on distal half. AR 0.32–0.35.

Thorax: Antepronotum with 4 lateral setae, median setae absent. Dorsocentrals 21–22; acrostichals 16–18 uni- to biserial, including 9–10 placed in front near the antepronotum, 7–8 distally; prealars 4–5. Scutellum with 4 setae in a single row. Preepisternum bare.

Wing (Fig. 1h, distal half): Brachiolum with 2 setae. Venation and distribution of setae on veins, membrane and cells: R, 7–8; R_1, 3–5; R_{2+3}, 9–11; An, 0; Cu_1, 0; r_{4+5}, 4; m_{1+2}, 3; m_{3+4}, 0; cu, 0; an, 0. Anal lobe weak. Squama with 1–2 setae. The distribution pattern of setae on wing cells is regarded as an important distinguishing feature to separate *T. spiesi* from other related species, especially *T. libanica*.

Legs: Spur of front tibia 23 μm long, spurs of middle tibia 35 and 23 μm long, spurs of hind tibia 13 and 15 μm long; hind comb with 12 setae. Fourth tarsus (ta_4) on PI distinctly bilobed apically, on PII and PIII weakly bilobed. Length (μm) and proportions of legs:

	fe	ti	ta_1	ta_2	ta_3	ta_4	ta_5	LR	BV	SV	BR
PI	275	310	137	91	66	43	49	0.44	2.90	4.27	1.8
PII	325	316	161	83	75	46	48	0.51	3.10	3.98	1.0
PIII	331	322	162	86	71	47	46	0.50	3.26	4.03	1.1

Hypopygium in dorsal and ventral view (Fig. 2a): Anal point 17–18 μm long; tergite IX 61–66 μm wide, broad with a nearly straight basal margin, bearing 9–10 setae (4 to 5 on each side of the anal point). Laterosternite IX with 2 setae. Transversal sternapodeme and phallapodeme as in Fig. 2a. Virga (Fig. 2b) semicircular and faint. Gonocoxite 112–115 μm long, maximum width 55 μm; inferior volsella (Figs. 2a, 2c) 7–8 μm long, 6–7 μm wide, nose-shaped, outer ventral margin straight, not swollen basally. Gonostylus (Fig. 2a) 57–63 μm long, triangular with pointed apex, bearing 5 or 6 stout orally directed setae; crista dorsalis swollen proximally; megaseta 8–10 μm long, slightly curved apically.

Female imago (Figs. 3a–e)
(n = 2, pharate adult females)

Colouration: as in the male adult except for the legs, which are brownish to dark brown including femora,

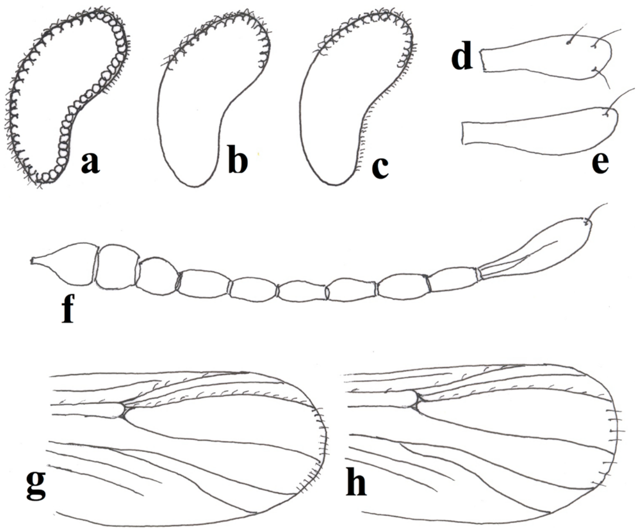

Fig. 1 *Thienemannia* spp. Hairs on inner margin of eyes: *T. spiesi* sp. nov. (a); *T. libanica* (b), Lebanon; *T. corsicana* (c), Corsica. Last flagellomere of antenna of: *libanica* (d); *spiesi* (e). Antenna of *T. spiesi* (f). Distal half of wing (g–h) of: *libanica* (g); *spiesi* (h).

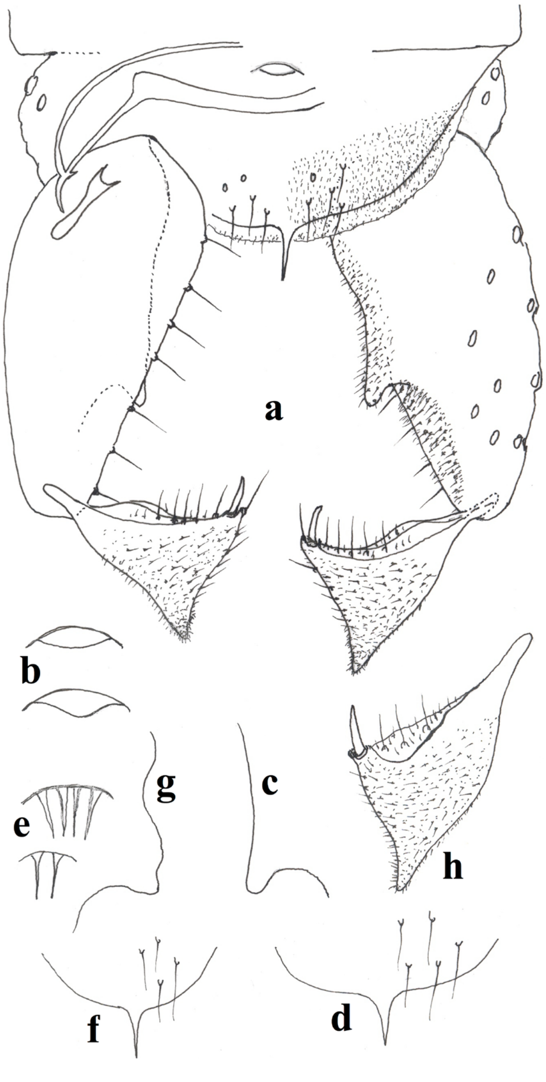

Fig. 2 Male imago of *Thienemannia* spp. *T. spiesi* sp. nov. (a–d): hypopygium, ventral, left and dorsal, right (a); Virga (b); inferior volsella (c); tergite IX and anal point (d). *T. libanica*: two aspects of virga (e); tergite IX and anal point (f); inferior volsella (g); gonostylus (h).

tibia and tarsi. Total length 1.50–1.60 mm. Wing length 1.20–1.30 mm. Antenna length 0.165–0.175 mm.

Head: Eyes hairy, hairs present on median part of inner eye margin; temporal setae 4, including 1 inner and 3 outer verticals, postorbitals absent. Clypeus with 8 setae. Antenna (Fig. 3a) 5-segmented; length (μm) of segments: 31, 33, 26, 30, 55; ultimate flagellomere moderately clubbed, bearing 1 apical seta; AR 0.18.

Thorax: Antepronotum with 2 lateral setae, median setae absent; acrostichals 17, relatively long, starting close to antepronotum; dorsocentrals 7; prealars 6. Scutellum with 6 setae in a single row. Preepisternum bare.

Wing: Brachiolum with 2 setae. Distribution of setae on veins, membrane and cells: R, 14; R_1, 26; R_{2+3}, 5; R_{4+5} 13; Cu_1, 4; An, 9; r_{2+3}, 0; r_{4+5}, 23; m_{1+2}, 4; m_{3+4}, 3; cu, 0; an, 0. Anal lobe weak. Squama with 2 setae.

Genitalia in dorsal and ventral view (Figs. 3b–e): Notum with distinct rami. Gonapophysis VIII (Figs. 3b–c); dorsomesal lobe (Fig. 3b) straight, ventrolateral lobe (Fig. 3b) large; apodeme lobe (Fig. 3c) sickle-like; gonocoxite (Fig. 3d) slightly elongated, bearing 5–6 setae; tergite IX (Fig. 3e) nearly semi-circular with 9 setae; sternite VIII with 8 setae. Seminal capsules 75 μm long, 51 μm wide, pear-shaped. Spermathecal ducts with loops and separate openings.

Pupal exuviae (Figs. 4a–d)

(n = 4)

Colouration: yellowish to yellow brown in general; thorax, yellowish brown with faint brown granulations near thoracic suture and dorsocentral area; antennal and wing sheaths with faint brownish shading; abdomen including anal segment brownish; with brownish apophyses; anterior area of tergites III–VIII brownish. Total length 1.40–1.50 mm.

Cephalothorax (Figs. 4a–b): Frontal apotome (Fig. 4a) slightly rugulose, frontal setae 13–15 μm long. Postorbitals and vertical minute and weak. Thoracic horn absent. Median antepronotals 23 and 33 μm long; precorneal setae 28, 33 and 21μm long. Dorsocentrals 9–12 μm long, inserted as in Fig. 4b; Dc2-Dc4 inserted close together; distance between Dc1 and Dc2, 61 μm; Dc2, Dc3 and Dc4 equidistant, each separated by about 9 μm.

Abdomen (Figs. 4c–d): Armament and distribution pattern of shagreen, patch of spines and spinules, chaetotaxy and lateral setation of segments as in Fig. 4c. Tergite I bare. Posterior transverse tooth row present on tergites III–VIII; tooth row on tergite II–VIII consists of 21–27 teeth in one continuous row; in general, teeth are mostly rounded at apices. Tergites II–III without anteromedian patch of shagreen or circular rows of spinulae. Transverse anterior shagreen present on tergites III–VIII consisting of spinules (III–VI), which increase medially to larger sized spines on tergites VII and VIII (8–10 spines on anterior part of tergite VII; 21–23 anteriorly and medially on tergite VIII). Anterior median circular patch of strong spinules present only on tergites VIII–IX; patch of strong spines and rows of spinules are connected on tergites VII and VIII. Sternites I–VIII bare. Conjunctives of intersegments I-VII with rows of anteriorly directed, long pointed spinules (Figs. 4c–d). Pedes spurii A and B absent. Lateral abdominal setae weak and hair-like,

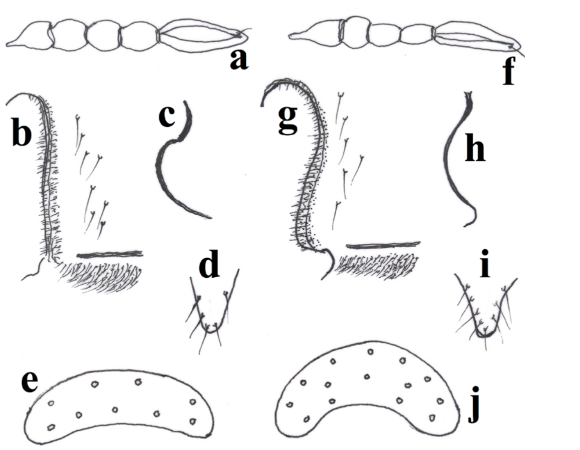

Fig. 3 Female imago of *Thienemannia* spp. *T. spiesi* sp. nov. (a-e): antenna (a), gonapophysis VIII, dorsomesal, ventrolateral and apodeme lobes (b); apodeme lobe (c); gonocoxite (d); tergite IX in dorsal view (e). *T. libanica* (f–j): antenna (f); gonapophysis VIII, dorsomesal, ventrolateral and apodeme lobes (g); apodeme lobe (h); gonocoxite, (i); tergite IX (j).

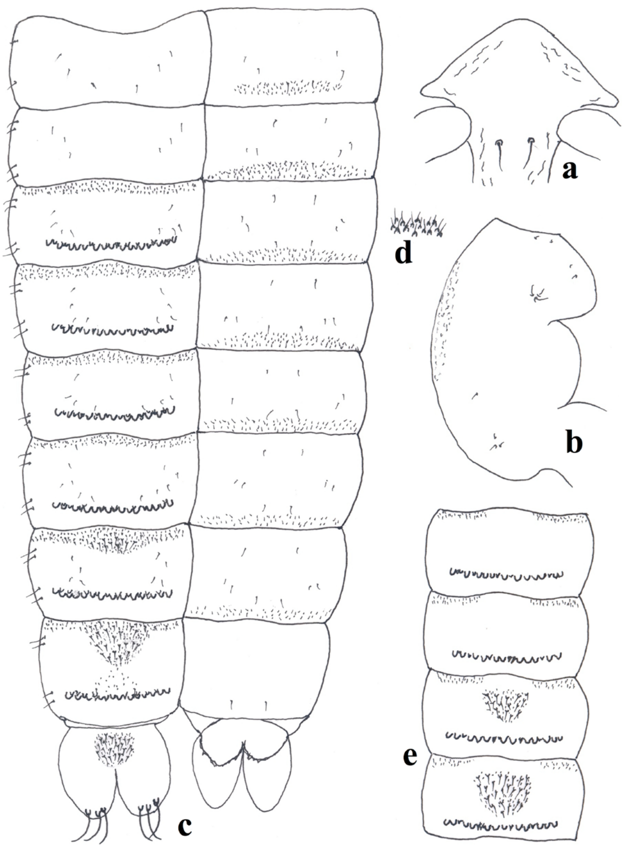

Fig. 4 *Thienemannia* spp. Male pupal exuviae of *T. spiesi* sp. nov. (a–d): frontal apotome (a); cephalothorax (b); abdominal segments I–IX with armament of tergites (left) and sternites (right) (c); details of transversal rows of orally directed long pointed spinules on conjunctives of intersegments II–VII (d). *T. libanica*: armament of tergites V–VIII (e).

consisting of reduced minute setae: tergite I with 2 setae, tergites II–VIII each with 4 setae. Apophyses brownish and relatively straight. Anal lobe 123–125 µm long, apical margin rounded; macrosetae 65–67 µm long, stout and slightly curved distally as in all *Thienemannia* pupal exuviae (Sæther 1985). Genital sac 63–67 µm long, rounded apically.

Taxonomic Position

The most important diagnostic features used to distinguish species in the genus *Thienemannia* genus are: chaetotaxy of the wing including the wing membrane; shape and form of the hypopygium including that of the virga, tergite IX, inferior volsella and gonostylus.

In the male adult, distinguishing characters between *T. spiesi* and *T. libanica* include: presence of hairs on proximal area of inner lateral margin of eye in *T. spiesi* (Fig. 1a), bare in *T. libanica* (Fig. 1b); last flagellomere elongated in *T.* spiesi (Fig. 1e), distinctly clubbed in *T. libanica* (Fig. 1d); chaetotaxy of cells r_{4+5} and m_{1+2} are different in the two species (Fig. 1h, *T. spiesi*; Fig.1g, *T. libanica*); virga not toothed in *T. spiesi* (Figs. 2a–b), bearing 2–4 spines in *T. libanica* (Fig. 2e); tergite IX wide, with a more or less straight basal margin in *T. spiesi* (Fig. 2d), rounded and tapered in *T. libanica* (Fig. 2f); inferior volsella nose-shaped in *T. spiesi* (Fig. 2c), swollen in *T. libanica* (Fig. 2g); outer margin of inferior volsella straight in *T. spiesi* (Fig. 2c), sinuous in *T. libanica* (Fig. 2g); crista dorsalis distinctly present on proximal part in *T. spiesi* (Fig. 2a), absent in *T. libanica* (Fig. 2h). In addition, the broad and more or less straight basal margin of tergite IX keys *T. spiesi* near both *T. gracilis* Kieffer, 1909 and *T. valespira*. (Moubayed-Breil and Ashe 2013, Figs. 14–15). However, a narrowed and tapered basal margin of tergite IX is found in both *T. libanica* (Fig. 2f) and *T. corsicana* (Moubayed-Breil 2013, Fig. 7).

In the female adult *T. spiesi* is separated from its sister species *T. libanica* by the following characters: the distribution of setae on wing veins, membrane and cells is quite similar to that in *T. libanica* but their number is much lower in *T. spiesi*; ventrolateral and dorsomesal lobes straight in *T. spiesi* (Fig. 3b), swollen distally in *T. libanica* (Fig. 3g); tergite IX semi-circular in *T. libanica* (Fig. 3j), less convex in *T. spiesi* (Fig. 3e).

The pupal exuviae of *T. spiesi* is distinguishable from other related species (especially *T. libanica, T. corsicana* and *T. valespira*) by the following characters: suture of pupal thorax bearing faint granulations in *T. spiesi* (Fig. 4b), bare in *T. libanica*, densely granulated in *T. corsicana* and *T. valespira*; anterior-median patch on tergite VII includes spinules and a few spines in *T. spiesi* (Fig. 4c), while spines are lacking in *T. corsicana* (Moubayed-Breil 2013, Fig. 12) and in *T. libanica* (Fig. 4e); transverse anterior rows of shagreen on tergites III-VIII continuous in *T. spiesi, T. corsicana* and *T. valespira* while it is interrupted medially in *T. libanica* (Fig.4e). The median patch of spines on tergite VIII in *T. spiesi* (Fig.4c) is connected to the anterior row of shagreen while in *T. libanica* (Fig. 4e) they are disconnected and the anterior row of shagreen is interrupted.

Ecology and Distribution

Thienemannia spiesi sp. nov. is currently known only from the Nationalpark Berchtesgaden in Bavaria, Germany. This new species is typically crenophilous and confined to helocrenes where shady and fresh habitats are characterized by a siliceous substratum and a low water conductivity value (Cd, 10–13µS/cm). Larvae of this new species are typically rheophilic occurring in running water of a spring in Bavaria. Two other orthoclad species, *Heterotrissocladius zierli* Stur and Wiedenbrug, 2005 and *Tavastia alticrista* Stur and Wiedenbrug, 2005, have been described from another spring in the same national park in Bavaria (Stur and Wiedenbrug 2005). The general description of the type locality where the associated pharate adult material was collected is detailed in a recent paper by Gerecke et al. (2011). Comparative ecological data given for *T. libanica* shows that this species, from Chlefa in Lebanon, is a typically rhithrobiontic species inhabiting karstic water with a high water conductivity value (Cd, up to 300 µS/cm).

Thienemannia spiesi sp. nov. from Germany has been confused with *T. libanica* due to the strong resemblance between their respective pupal exuviae. However, *T. libanica* is only known with certainty from a single locality in Lebanon: the upper stream of Yammouna-Chlefa (altitude 1,100–1,200 m), which is located in the inner plain of Bekaa (Laville and Moubayed 1985). Despite extensive investigations made throughout Lebanon, *T. libanica* is still unknown and apparently absent from coastal high mountain streams located in the eastern Mediterranean, including the Levantine Province. Further doubtful and probably misidentified records of *T. libanica* have been reported, based on pupal material, from some areas located in northern, central and southern Europe (Serra-Tosio and Laville 1991, zone E4; Moubayed et al. 2000, zone 3; Moubayed-Breil 2008, zones 5b and 10; Schacht 2010; Ashe and O'Connor 2012; Fauna Europaea, Sæther and Spies 2013). Therefore, some records of *T. libanica* from Europe may refer to *T. valespira*, *T. spiesi* sp. nov or some other related species. Occurrence of this new rheophilic species in a helocrene in Bavaria (Germany) indicates that it may be more widespread in cold high mountain springs and streams of central and southern Europe and therefore can be expected from such habitats in, for example, Austria, Switzerland, Italy and Spain.

Associated species encountered in the same locality include cold stenothermic and crenophilous elements (considered as typical helocrene species by Thienemann 1954, Lindegaard 1995, Stur and Wiedenbrug 2005, Moubayed-Breil and Ashe 2012) are: *Diamesa cinerella* (Meigen 1835), *D. macronyx* (Kieffer 1918), *Bryophaenocladius nidorum* (Edwards 1929), *B. subvernalis* (Edwards 1929), *B. vernalis* (Goetghebuer 1921), *Chaetocladius dissipatus* (Edwards 1929), *C. laminatus* (Brundin 1947), *C. suecicus* (Kieffer 1916), *Heterotrissocladius zierli*, *Parakiefferiella gracillima* (Kieffer 1922), *Metriocnemus eurynotus* (Holmgren, 1883), *Rheocricotopus effusus* (Walker 1856), *Tavastia alticrista*, *Tvetenia bavarica* (Goetghebuer 1934), *Micropsectra mendli* (Reiss 1983) and *M. sofiae* (Stur and Ekrem 2006).

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