INTRODUCTION

The concept of ecosystem services was defined by Daily (1997) as “the conditions and processes through which natural ecosystems, and the species that make them up, sustain and fulfil human life”. In particular, the Millennium Ecosystem Assessment (MEA, 2005) framework has defined four types of ecosystem services: 1) supporting services such as those controlling nutrient cycling and soil formation; 2) regulating services, such as those controlling superficial water flows and evapotranspiration; 3) provisioning services, such as those supplying food and water; and 4) cultural services, such as those offering recreational, and non-material benefits (Harrison & Ronald, 2010).

Several studies have pointed out the role played by biodiversity in ecosystem processes and services, as well as in human well being (Manes et al., 2012); however, biodiversity itself is influenced by global change factors. Modelling and evaluation of ecosystem service provision can be properly supported by spatially explicit studies at the landscape level using the ecoregion concept (Costanza et al., 2007; Nelson et al., 2009).

Until now the study of ecosystem services has not given much attention to plant-atmosphere relationships. For example, Costanza et al. (1997) have estimated the global economic value of seventeen ecosystems services to be up to $33 trillion per year, among these, only two are the ecosystem services related to the atmospheric compartment. Recently, Liu et al. (2010) have pointed out the necessity to include the concept of natural capital in the economy of...
human society in order to have objective economic basis on which to base the preservation of the ecosystem functions. In this context, the role of the forests to reduce the tropospheric ozone ($O_3$) levels should be an important aspect to be considered in the global evaluation of their economic evaluation in terms of ecosystem services. $O_3$ is a secondary pollutant formed in the atmosphere as a result of the reaction between the primary pollutants nitrogen oxides (NOx) and volatile organic compounds (VOC), under conditions of high irradiance (Jenkin & Clemitshaw, 2000). Because of the increasing emissions of NOx and VOCs from combustion processes of anthropogenic origin, $O_3$ concentrations have increased by 36% worldwide since the onset of pre-industrial era (Vingarzan, 2004). Despite substantial efforts in control and mitigation initiatives that, in recent years, have reduced the intensity and the frequency of $O_3$ peaks, the background concentrations of this pollutant are increasing in both industrialized and developing countries (Ashmore, 2005; Coll et al., 2009), thus posing a concrete risk to human health, natural vegetation and crop species (Mills et al., 2011a). Current European legislation about $O_3$ (Directive 2008/50/EC) establishes that the target value for protecting human health is 120 µg/m$^3$, not to be exceeded on more than 25 days per calendar year averaged over three years (averaging period: maximum daily eight-hour mean). Nonetheless, the $O_3$ concentrations in Europe often exceed this threshold, particularly in Mediterranean areas, where summer climatic conditions characterized by high temperatures and strong irradiances favour the $O_3$ formation (EEA, 2012).

The increasingly evident effects of $O_3$ on human health and on ecosystems have underlined the need to develop environmental policies to reduce the air concentrations of this oxidizing agent. Considering that $O_3$ can be transported over long distances, and that under certain meteorological conditions high $O_3$ concentrations can affect vast areas of Europe, an integrated international approach must be adopted for the first time by the United Nations Economic Commission for Europe (UNECE), and in 1979 the Convention on Long-Range Transboundary Air Pollution (CLRTAP) was launched. In 1988, the International Cooperative Programme on Effects of Air Pollution and Other Stresses on Agricultural Crops (ICP Crops, currently known as “ICP Vegetation”), as well as the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) were launched. Under the CRLTAP, numerous efforts have been made to establish $O_3$ concentrations above which negative effects on natural vegetation and crops can occur (Fuhrer et al., 1997). The critical level for a pollutant is defined as the concentration above which harmful effects can occur for receptors such as plants, ecosystems, and materials (UNECE, 1998). These critical levels serve as “targets” for developing policies aimed at decreasing atmospheric pollution, as well as for identifying risk areas using maps showing when the values exceed the thresholds both using the measured and modelled $O_3$ concentrations (Amann et al., 1995). Currently, Directive 2008/50/CE sets the limits of $O_3$ concentrations for plant protection on the basis of the AOT40, an index of cumulative exposure (Fuhrer & Achermann, 1994). This index corresponds to the sum of hourly $O_3$ concentrations over 40 ppb during daylight, when solar radiation exceeds 50 Wm$^{-2}$, and is calculated over a period of three months for crops and semi-natural species, and over the whole growing season for forests (UN/ECE Mapping Manual, 2011).

After more than 30 years of studies carried out by the CRLTAP Working Group on Effects, it is now well established that $O_3$ effects on plants are more related to the amount of $O_3$ that enters the leaf through stomata, i.e. the stomatal $O_3$ flux ($F_{O_3st}$), than to the mere $O_3$ concentration in air (Manes et al., 2005). $O_3$ enters in leaf tissues through stomata (Laish et al., 1989) and, as a consequence, the physiological parameters related to the degree of stomatal opening, such as the stomatal conductance ($g_s$), can predict plant $O_3$ uptake. Stomatal conductance is a key physiological variable, which is related to the leaf temperature, vapour pressure deficit, sub-stomatal CO$_2$ concentration, soil water potential, and irradiance (Chaves et al., 2002; Vitale et al., 2007). Many studies have shown that $O_3$ fluxes to plants and $O_3$ concentrations in the air are well correlated only when stomatal conductance is unconstrained by environmental factors. Instead, when $g_s$ is limited by drought or vapour pressure deficit, the sum of all daytime $O_3$ concentrations overestimates the $O_3$ flux (Gerosa et al., 2009). Given the effect of climatic factors in the amount of $O_3$ that is absorbed by the leaf, the stomatal flux of $O_3$ varies by geographic area, season, and time of day. Different geographic regions with similar AOT40 values can have considerably different values for $O_3$ flux (Zeller, 2002), and various studies have demonstrated that AOT40 is inadequate for estimating the loss of agricultural crops in Europe (Mills et al., 2011a). Thus, when using atmospheric $O_3$ concentrations as an indicator of uptake, there is a very high risk of systematic error, because any factor that influences stomatal conductance but not the environmental concentration of $O_3$ will not be detected (Vitale et al., 2005; Gerosa et al., 2009). In particular, in Mediterranean ecosystems, the use of AOT40 can lead to an overestimate of the effects of $O_3$ compared to other parts of Europe if the relation of exposure-response is not derived under these conditions (Manes et al., 2007). A good index of $O_3$ exposure should therefore be sensitive to the factors that influence stomatal conductance. Moreover, it should include a quantitative representation of the detoxification capacity of leaf tissues (Musselman &
Massman, 1999). For this reason, a completely new concept has been recently developed, the Phytotoxic Ozone Dose over a threshold flux of Y nmol m\(^{-2}\) of Projected Leaf Area s\(^{-1}\) (POD\(_Y\)). POD\(_Y\) can be described as the “effective dose” or “effective flux”, where Y represents a detoxification threshold, below which it is assumed that the O\(_3\) absorbed by the plant can be detoxified (Mills et al., 2011b).

The exchange of air pollutants between the atmosphere near the ground and the phytosphere is studied not only because it induces injuries on vegetation, but also because it is an important process affecting the pollutants concentration in the troposphere (Escobedo et al., 2011). In particular, the vegetation contributes to govern tropospheric O\(_3\) budget through three components of O\(_3\) fluxes: stomatal uptake, non stomatal deposition, and gas-phase reactions (Cape et al., 2009). The latter two processes in some cases are not distinguished, and referred to as “non stomatal processes” or simply “non stomatal flux”. The sum of these three components is usually referred as “total O\(_3\) flux” (FO\(_3\)tot). Different papers have reported that the total O\(_3\) flux from the atmosphere to canopy surfaces can have positive effects on air quality, and consequently to human health and wellbeing (Escobedo and Nowak, 2009; Manes et al., 2012). The quantification of this ecosystem service is therefore of particular interest, being also related to the functionality of vegetation, which, in its turn, is related to the occurrence of natural and anthropogenic stress factors.

The aim of this paper is to estimate the role of the main natural woody vegetation classes, considering the classes of the CORINE Land Cover Classification of the Latium Region (Central Italy) in removing tropospheric ozone during the growing season of the year 2005. This is a preliminary case-study, to give a contribution to the international debate about the estimation of the value of plant biodiversity as a natural capital.

**MATERIALS AND METHODS**

**Ecoregional context**

Ecoregions are broad geographic areas that display, at multiple and hierarchical levels, clearly distinct combination of bioclimatic, biogeographic and coarse physiographic features and vegetation potential. Though the ecoregion classification process of Italy is still in progress (Blasi & Frondoni, 2011; Blasi et al., 2011; Capotorti et al., 2012), the adoption of temporary boundaries for Ecological Divisions, Provinces and Sections however preserves its methodological significance. Lazio straddles between the Apennine Province of the Temperate Division and the Tyrrhenian Province of the Mediterranean Division (Figure 1). The Apennine Province is characterized by a Temperate climate; its potential natural vegetation (Blasi, 2010) prevalently consists of deciduous forests dominated by *Quercus pubescens*, *Q. cerris*, *Fagus sylvatica* and *Ostrya carpinifolia*. The Tyrrhenian Province is characterised by Mediterranean and Sub-Mediterranean climate; its potential natural vegetation prevalently consists of thermophilous, mainly deciduous forests dominated by *Quercus cerris*, *Q. frainetto*, *Q. virgiliana* and *Q. ilex*.

For the purposes of this study, we have divided the actual forest vegetation of each Ecoregional Province in two classes: deciduous and evergreen. In particular, deciduous forests include: deciduous oaks, mesophilous mixed woods, chestnut woods, beech woods, mixed coniferous-broadleaves woods with oaks prevailing, mesophilous species prevailing, and beech prevailing; evergreen forests include: holm oak and/or cork oak, Italian stone pine, Mediterranean maquis, mixed coniferous-broadleaves woods with holm oak and/or cork oak prevailing, with Italian stone pine prevailing.

**Methodological approach for the estimation of ozone removal by vegetation in the Latium Region, Italy**

On the basis of Interpolated maps showing air quality in Europe (AOT40 for forest 2005, http://www.eea.europa.eu/data-and-maps/figures/ozone-aot40-for-forest-2005), we have derived the mean daily O\(_3\) concentrations for the Latium region (Italy).

Stomatal O\(_3\) daily fluxes (FO\(_3\)stom\(=\) (O\(_3\)ext - O\(_3\)int) \(\times\) gs \(\times\) 0.613) (nmol m\(^{-2}\) s\(^{-1}\)) from April to September, for the two vegetation
classes analysed, were calculated using stomatal conductance (gs) data, estimated as described in Manes et al. (2012), and as reported in Borghetti and Magnani (1999).

Stomatal fluxes (FO3s(t)), following Gerosa et al. (2005), correspond to about 30% of total O3 flux:

\[
FO3cum = \left( \sum_{i=1}^{n} FO3s(t) \times Ph \times 3600 \times \frac{1}{0.289} \right) \times 10^6
\]

Where:
- FO3s(t) is the daily average O3 flux.
- Ph is the photoperiod duration in hours.
- 0.289 is the ratio of stomatal and total flux (Gerosa et al., 2005).

By a dimensional point of view, FO3cum is measured in g (or mol) per m² of soil covered by the given leaf-type vegetation, when [O3] is expressed in µg/m³ (or ppb).

Ozone cumulated fluxes (Mt/ha) was multiplied for the total surface coverage of every vegetation classes analyzed.

**Estimation of externalities values for each class**

Following Nowak et al. (2006), we have applied for O3 the estimation of 6752 U.S. dollars per metric ton as average externality value.

**RESULTS AND DISCUSSION**

The distribution of the land use classes, on the basis of the 4th Level CORINE Land Cover, regarding deciduous and evergreen forests in Latium Region is showed in Figure 2. The surface occupied by deciduous and evergreen forests is 361919.3 ha and 50819.0 ha, respectively.

![Figure 2. Distribution of the two considered vegetation classes (Deciduous and Evergreen) in the two Ecoregional Provinces of the Latium Region, on the basis of the 4th Level CORINE Land Cover.](image-url)
The value of total ozone flux of the two analyzed forest classes are reported in Figure 3, with three levels of total ozone uptake. Between the two forest classes, different values of cumulated ozone fluxes (t ha\(^{-1}\)) in both the Ecoregional Provinces, were obtained (Table 1). In particular, deciduous species show about double values of magnitude than evergreen species. This result may be attributable to higher ozone air concentration occurred in 2005 (Table 2), and to the differences of stomatal conductance as estimated with this study for the two vegetation classes.

![Figure 3. Total O\(_3\) flux (t) to deciduous and evergreen forests in the two Ecoregional Provinces of the Latium region.](image)

**Table 1.** Values of Total O\(_3\) flux (t), of Total O\(_3\) flux per hectare of forest cover (t/ha), and of Total O\(_3\) flux per hectare of Province (t/ha Province), estimated for deciduous and evergreen forests in the two Ecoregional Provinces of the Latium Region.

<table>
<thead>
<tr>
<th>PROVINCE</th>
<th>Surface (ha)</th>
<th>Vegetation class</th>
<th>Vegetation cover (ha)</th>
<th>Total O(_3) flux (t)</th>
<th>Total O(_3) flux (t/ha vegetation class)</th>
<th>Total O(_3) flux Province (t/ha Province)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apennine chain</td>
<td>816636.20</td>
<td>Deciduous</td>
<td>261045.3</td>
<td>8478.7</td>
<td>0.0325</td>
<td>0.0104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evergreen</td>
<td>21746.5</td>
<td>338.7</td>
<td>0.0156</td>
<td>0.0004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>282791.8</td>
<td>8817.4</td>
<td>0.0481</td>
<td>0.0108</td>
</tr>
<tr>
<td>Tyrrhenian Borderland</td>
<td>906206.88</td>
<td>Deciduous</td>
<td>100874.0</td>
<td>3314.0</td>
<td>0.0329</td>
<td>0.0037</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evergreen</td>
<td>29072.5</td>
<td>461.3</td>
<td>0.0159</td>
<td>0.0005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total</td>
<td>129946.5</td>
<td>3775.3</td>
<td>0.0487</td>
<td>0.0042</td>
</tr>
</tbody>
</table>
Cumulated O₃ fluxes data allowed to estimate the externality value of this ecosystem service provided by forests: in the Apennine Chain Province, $57,248,431$ and $2,286,567$ for deciduous and evergreen forests, respectively, and in the Tyrrhenian Province, $22,376,136$ and $3,114,686$ for deciduous and evergreen forests, respectively. This corresponds, for the growing season 2005, to a total value of $85,025,821$ attributable to the ecosystem service of tropospheric O₃ removal provided by the natural forests of the Latium region. From this calculation, it is possible to show that deciduous species give the major contribution, estimated as $93.6$ % of the total value.

Since the two considered Provinces have a widely spread potential for deciduous forests, even if termophilous in the Tyrrhenian one (Fig. 4), the regulating service of O₃ removal could be here improved by promoting and facilitating natural vegetation recover according to the mainly deciduous vegetation potential.

On the basis of standard woody value estimation (INEA, 2012), it was calculated the yearly rate return relative to the natural capital of two vegetation classes, which is, for the ecosystem service of tropospheric classes, about 0.6%.

This study takes into account only a process provided by forest ecosystems, related to the links between structure and functions of the two different vegetation classes examined. We acknowledge that there are some uncertainties in producing such estimates, however, these data are a first contribute to monetize ecosystem services of regional and national forests in Italy, and more in general, to promote the use of ecosystem service valuation in forest management and environmental policy-making, to highlight their intrinsic and utilitarian roles. Finally, the externality value used in our estimation does not take into account the positive effects on human health and wellbeing deriving from the ozone removal potential of forests in rural and periurban areas.

### Table 2. Percentage cover of Evergreen and Deciduous forests for each AOT40 class. The mean stomatal conductance (gₛ, mol m⁻² s⁻¹) for each vegetation type in each AOT40 class is also reported. AOT40 classes: 1 = from $25172.4$ to $31515.5$ µg m⁻³; 2 = from $31515.6$ to $35847.3$ µg m⁻³; 3 = from $35847.4$ to $44799.9$ µg m⁻³.

<table>
<thead>
<tr>
<th>AOT40 class</th>
<th>Vegetation class</th>
<th>% Cover for each AOT40 class</th>
<th>Mean gₛ (mol m⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Deciduous</td>
<td>31.6</td>
<td>0.172</td>
</tr>
<tr>
<td>1</td>
<td>Evergreen</td>
<td>18.2</td>
<td>0.084</td>
</tr>
<tr>
<td>2</td>
<td>Deciduous</td>
<td>36.8</td>
<td>0.172</td>
</tr>
<tr>
<td>2</td>
<td>Evergreen</td>
<td>40.9</td>
<td>0.083</td>
</tr>
<tr>
<td>3</td>
<td>Deciduous</td>
<td>31.6</td>
<td>0.172</td>
</tr>
<tr>
<td>3</td>
<td>Evergreen</td>
<td>41.0</td>
<td>0.083</td>
</tr>
</tbody>
</table>

Figure 4. Potential Natural Vegetation of Latium Region. Vegetation potential is represented according to the physiognomic character of the main vegetation series (originally redrawn from Blasi 2010).
REFERENCES


ecosystem services. Theory, practice, and the need for a
transdisciplinary synthesis. Annals of the New York
Academy of Sciences 1185, 54–78.

Manes F., Incerti G., Salvatori E., Vitale M., Ricotta C.,
and stability of tropospheric ozone removal. Ecological
Applications 22(1), 349–360.

tropospheric ozone impact on plants in natural and urban
areas with a Mediterranean climate. Plant Biosystems 139,
265–278.

Estimates of potential ozone stomatal uptake in mature trees of
Quercus ilex in a Mediterranean climate. Environmental
and Experimental Botany 59, 235–241.

Millennium Ecosystem Assessment (MEA) 2005.
Ecosystems and Human Wellbeing: Synthesis. World
Resources Institute. Island Press, Washington, DC.

Mills G., Hayes F., Simpson D., Emberson L., Norris D.,
Harmens H., Büker P., 2011a. Evidence of widespread
effects of ozone on crops and (semi-)natural vegetation in

Mills G., Pleijel H., Braun S., Büker P., Bermejo V., Calvo E.,
Danielsson H., Emberson L., González Fernández I.,
Grünhage L., Harmens H., Hayes F., Kerlsson P-E.,
Simpson D., 2011. New stomatal flux-based critical levels
for ozone effects on vegetation. Atmospheric Environment
45, 5064–5068.

Musselmann R.C., Massmann W.J., 1999. Ozone flux to
vegetation and its relationship to plant response and ambient
air quality standards. Atmospheric Environment 33, 65–73.

Nelson E., Mondoza G., Regetz J., Polasky S., Tallis J.,
Cameron D.R., Chan K.M.A., Daily G.C., Goldstein J.,
Kareiva P.M., Londsdorf E., Naidoo R., Ricketts T.H., Shaw
M.R., 2009. Modelling multiple ecosystems services,
biodiversity conservation, commodity production, and
tradeoffs at landscape scale. Frontiers in Ecology and
Environment 7(1), 4–11.

Nowak D.J., Crane D.E., Stevens J.C., 2006. Air pollution
removal by urban trees and shrubs in the United States.
Urban Forestry and Urban Greening 4, 115–123.

Working Group on Ozone Directive and Reduction Strategy
Development.