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Knowledge dynamics and sources of eco-innovation: Mapping the Green Chemistry community

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Abstract

Over the last few decades, the interest for developing a more sustainable chemistry has increased worldwide and has triggered the proliferation of new knowledge. The present article aims at investigating the dynamics of scientific knowledge underlying this emergent field, the main countries and organizations involved, and the factors that have shaped the evolution of the field. In order to circumscribe such a still fluid area of research, we first show how an epistemic community around the concept of Green Chemistry (GC) has emerged and materialized. We then build an original dataset of scientific publications generated by this community and apply two algorithms for the analysis of citation networks. That allows us to identify and analyze the scientific knowledge that laid the foundations of the GC community and the main scientific trajectory that emerged along its whole evolution. The results highlight that the GC community, strongly supported by the US EPA, has grown exponentially since 2000 and has spread among a wide range of countries, including emerging countries. The results also suggest that policy and industry interests, as well as regulation, have played a significant role in shaping the emergence and evolution of GC.

Keywords: eco-innovation; green chemistry; scientific knowledge dynamics; epistemic community; citation network analysis.

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1. Introduction

A grand challenge facing modern economy is to move towards more sustainable systems of production and consumption. Addressing this challenge will require to modify the relationship with natural resources, to rethink the ways of producing and using materials, and finally to call into question patterns of consumption. On the supply side, this transition toward more sustainable systems mainly depends on eco-innovation, i.e., the ability of firms to develop new methods, products and/or processes which benefit the environment and contribute to environmental sustainability [1].

Within this perspective, the chemical industry has a leading role to play. This is indeed an important sector in many countries, in terms of both economic growth and employment, and its products, from oil to medicines, are widely spread. However, the chemical industry is also one of the biggest sources of pollution, environmental risk and hazard. It is energy-intensive, it is responsible for producing, using and transporting many harmful substances, and chemical products are largely created using non-renewable, petroleum-based resources as feedstocks. The chemical industry also releases more hazardous waste to the environment than any other sector, and more in total than is released by the next nine sectors combined [2]. For those reasons, the sector is characterized by very stringent environmental regulation, which can take the form of product bans that impede the use of harmful chemical inputs in the production process itself, thus forcing chemical producers to look for alternative substances and changing the traditional production practices [3].

As a consequence of the impact on human and environmental health of traditional chemical products and processes, the interest for developing a more sustainable chemistry has increased worldwide over the last few decades and has triggered the proliferation of new knowledge, which has taken a multiplicity of appellations. Such a multiplicity is symptomatic of the fuzziness of the field: being this an emerging field, its boundaries are not well defined, in the community of practitioners there are different visions on “how to do things” and a variety of directions of search are currently explored.

Scientific research, often supported by government initiatives, has made a fundamental contribution to the development of this new way of doing chemistry. This is mainly due to the science-based nature of the chemical industry, which typically benefits from the important and direct contribution of scientific advances for innovating [4]. In spite of that, no systematic quantitative evidence has been yet provided in order to examine the scientific knowledge underlying the “movement” towards a more sustainable chemistry. The novelty of the present article is to fill that gap in the literature by addressing the following questions. How can we delineate the boundaries of this emerging scientific field? What are the most relevant scientific advances that are driving the evolution of the field? What are the main countries and organizations involved? What are the factors that have shaped the emergence and evolution of the field? The answers to those questions are relevant for understanding both the

technological trajectories that are moving towards a more sustainable chemistry and the sources of eco-innovation in the chemical industry.

In order to answer the mentioned questions, we first review the historical and specialized literature of the field, and interacted with the community of practitioners. On this basis, we show that despite the diversity of visions and approaches of practitioners, an epistemic community has emerged and materialized around the concept of Green Chemistry (GC). Second, we take the GC community as unit of our analysis, build an original dataset of scientific publications generated by this community and discuss the main trends emerging from its examination. In doing so, we highlight how GC knowledge evolved over time and spread among different scientific journals, disciplines and countries. Third, we further investigate GC knowledge by constructing a network of citations among GC publications and using two network analysis algorithms, namely the Hubs and Authorities algorithm and the Main Path algorithm. That allows us to identify and analyze the scientific knowledge that laid the foundations of the GC community and the main scientific trajectory that emerged along its whole evolution, as well as the countries and organizations involved in the generation of that knowledge. The analysis of the scientific knowledge selected by network analysis algorithms also allows us to discuss the factors that have shaped the emergence and evolution of the GC community.

The rest of the article is organized as follow. In section 2, we outline the historical evolution of GC and its main research areas. We then present the GC community, which is defined and characterized as an epistemic community. Section 3 illustrates the data and methods. Section 4 shows the results of our empirical analysis and discusses the factors that have shaped the GC community, as revealed by the study of scientific publications selected by the network analysis algorithms. Section 5 concludes.

2. Background

2.1. The historical evolution of GC

Under societal and political pressures, the last few decades have witnessed the emergence of new knowledge aimed at developing a more sustainable chemical industry. In the 1980s, several environmentally conscious terms, like clean chemistry, environmental chemistry, green chemistry, benign chemistry and sustainable chemistry, entered the chemical arena, and still today scientists use a variety of terms to qualify sustainability research in chemistry, talking about bio-based chemistry, biomass chemistry, decarbonised chemistry, renewable carbon chemistry etc.. Such a multiplicity of terms, whose boundaries are not precisely defined, is symptomatic of the fuzziness of the field and of the different visions underlying such an emergent area of research.

Despite that diversity of terms and visions, a Green Chemistry movement came out and materialised, strongly supported by a network of professionals from the academic, industry and policy spheres. That is also shown by the rapid growth, since 1998, of term “green chemistry” in scientific publications (see Figure 1 in the Appendix) and in public debate. Linthorst [5] provides an historical analysis of the origins and development of GC, stressing a three-stage process of construction. The first period goes from the 1980s until end of 1993 and is characterized by the need for adopting pollution prevention, rather than a command and control policy, at the level of the US Environmental Protection Agency (EPA). This new approach was politically formalized in the Pollution Prevention Act of 1990, which outlined the shared interest of government and chemical industry to cooperate and opened financial means to EPA for launching new programs aimed at developing alternative synthetic designs.

The second period [1993-1998] is marked by a movement of progressive institutionalization of GC. A symposium was organized to allow networking and cooperation between industry, academia and government, but also between nations like Japan and Italy. During these years, the terminology started to change in favor of the term green chemistry (compared to benign chemistry for example). In 1998, Prof. Paul Anastas, who is also an EPA representative, and John Warner published the first handbook on GC [2], in which they expose the GC objectives, visions and challenges. Here, the authors define GC as the “*design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances*” and illustrate the 12 principles of GC, a set of “*design rules*” to help chemists developing the GC². Linthorst [5] notes that this handbook clearly results from a politically supported network originating from the US. Political support of the concept of GC continued in the following years, taking the form of the US Presidential GC Challenge Awards (1995), the GC Institute (a non-profit organization funded in 1997 and aimed at the incorporation and dissemination of GC principles), the GC Network (1998), and the GC Journal (1999), a scientific journal explicitly focused on GC research.

The third period [1999-2008] is characterized by a significant contribution of the GC Journal in terms of output. In 2009, its tenth year of publication, the GCJ was ranked #15 out of 140 chemistry journals according to highest impact factor³. Networking activities, special issues, conferences and a continuous political support were all drivers for the growth of GC in this period. It is also important to note that, since the beginning, the EPA put particular emphasis on promoting networking and cooperation between academic science and industry in the design and implementation of GC principles. Far from being confined in the US, GC initiatives have multiplied around the world, especially in Japan, Europe, Australia, Canada and China [6]. These initiatives have taken many forms (networks, specialized research centers, curricula, summer schools), and most of the time they are part of a wider regulatory framework that supports sustainability research in chemistry. In Europe, for example, the

² The list of the 12 principles of GC is contained in the Appendix.

³ ISI Web of Knowledge, Journal Citation Report.

entry into force on June 1 2007 of the European Community Regulation on chemicals and their safe use (EC1907/2006), also called REACH, contributes to a larger movement in favor of a more sustainable chemistry and seems to translate into law some of the main objectives of GC [7].

2.2. The main areas of GC research

By reviewing the specialized literature on GC⁴ and interacting with the community of practitioners⁵, we have identified the following main areas of GC research.

2.2.1. *Alternative or renewable feedstocks*

One of the major goals of GC is to produce chemical feedstocks in a more sustainable way, using annually renewable raw materials instead of fossil resources like oil, coal and natural gas. This research is driven not only by the need of reducing the high environmental impact of existing chemical feedstocks, but also, and more importantly, by the expected increase of energy demand and depletion of fossil resources. The main alternative solutions currently explored relate especially to agricultural products, i.e., the biomass derived from plants. Carbohydrates, lignin, natural oils, soy and chickens are examples of biomass that, together with agricultural waste and non-food-related bioproducts (which are often made up of lignocellulosic materials), are already used in a variety of applications, ranging from biofuels to biopolymers. Biopolymers are new polymer materials based on biological feedstocks that are currently used for producing recyclable and/or biodegradable commercial plastics (e.g., polysaccharides, chitin and chitosan). Besides, the development of integrated biorefineries – in which energy, chemicals, and food processing are combined – is considered of crucial importance for extracting the maximum value from biomass and meeting the goals of sustainability. CO₂ and other gases like hydrogen and methane are also being studied as alternative solutions to traditional feedstocks.

2.2.2. *Alternative solvents*

Another important area of GC investigation focuses on searching alternative media in which to carry out synthetic transformations (chemical reactions). Solvents have always been considered the dominant media, both in the chemical industry and in academic research, because of their excellent solvency properties in a wide range of reactions. The counterpart is that solvents account for the vast majority of mass wasted in syntheses and processes. Moreover, many conventional solvents are toxic, flammable or corrosive and their volatility contributes to air pollution (Volatile Organic Compounds),

⁴ We relied in particular on [2] and [8-12].

⁵ We interviewed researchers from the Laboratoire de Chimie des Polymères Organiques (LCPO), University of Bordeaux I, and participated to two focus groups organized by Prof. Martino Nieddu at the University of Reims within the ANR research program "Une Approche Economique de l'intégration des dimensions socio-économiques et techniques dans les Programmes de Recherche en Chimie Doublement Verte".

increases the risk of worker exposure and is responsible for industrial accidents. GC research on alternative reaction media is moving along three main directions: 1) developing new reaction processes that do not use solvents at all, the so-called solvent-free reactions; 2) designing more biodegradable and/or recyclable solvents; 3) inventing new environmentally benign solvents. In this regard, the major alternative solvents explored are: 1) supercritical fluids, in particular supercritical CO₂, which has been used for example in the decaffeination of coffee bean, 2) ionic liquids (organic salts that are liquid at room temperature); 3) water.

2.2.3. *Alternative synthetic pathways*

The 12 principles of GC also call into question the traditional way of performing chemical reactions. In this regard, GC research is mainly focusing on searching greener alternatives to metallic, and generally highly polluting catalysts. These alternatives include the development of organocatalysts, which are catalysts based on organic compounds, and biocatalysts, i.e., natural catalysts such as “modified” enzymes. Biocatalysis, which has become known as white biotechnology (to distinguish it from red and green biotechnology for medical and agricultural applications, respectively), has undergone explosive growth [12]. For example, enzymes have completely displaced conventional catalysts as a low-cost option in the manufacture of several generic pharmaceuticals. In addition to being green catalytic processes that are performed at ambient temperature and pressure, often in water as solvent, the catalysts themselves (enzymes) are biocompatible, have low ecotoxicity and are produced from natural, renewable raw materials. Another area of GC inquiry regards the so-called biomimetic catalysis, a bio-inspired synthesis that can be used to produce with minimal solvent, chemical and energy waste, a number of materials like conducting polymers and non-toxic industrial antioxidants. GC research efforts are also directed towards both the design of more selective catalysts to reduce the number of stages in a given process (e.g., ibuprofen and Zolofit) and the development of reusable or recyclable catalysts.

2.2.4. *Alternative industrial processes and reactors (chemical engineering)*

The development of greener industrial processes and reactors is another important area of GC research. The goal is to design eco-efficient processes that minimize waste and are simultaneously safer, less toxic and energy efficient. In this perspective, process intensification is of crucial importance since, in this way, the ratio between reactors size and production capacity can be reduced, and equipment can be miniaturized, the so-called microreactors. Microreactors (in which reaction components are manipulated in channels as small as 10 µm in diameter) enable to enhance yield and selectivity of reactions. Switching from batch reactions to continuous processing also can offer important advantages. Continuous processing is not only safer, but can often give a higher-purity product [12]. Alternative techniques like microwave-, sono-, or photo- assisted chemistry have been developed and applied as well by green chemists in order save energy, reduce reactions times, simplify experimental

conditions and increase the effectiveness of catalysts. In parallel, one of the 12 principles of GC calls for improved monitoring of chemical syntheses and processes to prevent waste, reduce the use of solvents and minimize the formation of hazardous side products. This has led to the development of the so-called “green analytical chemistry”, which is based on the use of technologies involving real-time, in-process monitoring and control prior to the formation of hazardous substances.

2.3. GC as an epistemic community

The historical development outlined in section 2.2 enables us to understand how an epistemic community around GC has come into being. The concept of epistemic community has gained ground in political science, particularly in international relations, following the publication of the seminal paper by Haas [13]. This author defines an epistemic community as “*a network of professionals with recognized expertise and competence in a particular domain and an authoritative claim to policy-relevant knowledge within that domain or issue-area*”. According to this perspective, epistemic communities produce knowledge as much as they set to influence politics. Epistemic communities emerge from a policy demand and the policy receptivity is a crucial issue for them: they have to produce “usable knowledge” and the knowledge they produce has to provide solutions in response to specific problems. Such communities are also associated to a common cognitive structure enabling a shared understanding and they typically rely on a procedural authority, explicit or not [14-16]. The procedural authority corresponds to a set of rules that define the objectives of the community and the means to implement them, but these rules also govern the collective behaviour within the community. Given the heterogeneity of the members of the community, one of the main tasks of an epistemic community is to create a codebook.

The concept of epistemic community is particularly relevant in the context of academic science since it offers a better understanding of academic relations and practices. In the academic sphere, epistemic communities are constituted around groups of researchers who share a common cognitive objective of knowledge creation in a common research field. The frontiers of epistemic communities evolve with the dynamics of research activities such that these communities can experiment evolution through a life cycle, going until the emergence and the death of a community. Given their characteristics and finalities, such communities contribute to the emergence of new knowledge areas, while promoting diversified and codified knowledge externalities, like publications, discoveries, new applications etc.. Epistemic communities of researchers acknowledge as procedural authority the submission of their work to peer reviewers. Rules and principles acknowledged by the community are essential elements of the codified knowledge. These are expressed in a formal language and transmitted through written medium: they represent the codebook of the community.

Based on that argument, we can argue that the socio-political construction of GC has been conducive to the emergence of an epistemic community characterised by the following aspects. First, a

group of chemists (forming networks) shares the common objective of knowledge creation in the field of sustainability research. Second, the handbook on GC written by Anastas and Warner [2] stands for the codebook of the community. It provides common challenges to chemists involved with the discovery, manufacture, and use of chemicals, offering a vision on how to move towards a more sustainable chemistry. Third, the 12 principles of GC summarize these common challenges and provide rules to accomplish them. In fact, such principles are viewed “*as a reflection of the science that has been done within this nascent field in the recent past, as well as a direction that has been set by some of the pioneering scientists who have laid the groundwork for the future*” [2]. Finally, the *Green Chemistry Journal* can be viewed as the procedural authority of the community. All these elements provide evidence for the existence of a GC epistemic community in which the US EPA, researchers like Anastas and Warner, as well as the *Green Chemistry Journal*, play an authoritative and structural role. This concept of epistemic community seems all the more relevant, compared to the more general concept of scientific community, since the development of GC is closely linked and supported by political institutions, in particular the US EPA.

We are aware that the concept of GC community does not capture the whole scientific knowledge generated in order to achieve a more sustainable chemical industry. As we have mentioned in section 2.2, there are different visions in the community of practitioners on “how to do things” and there are scientists that do not share the GC approach. However, to the best of our knowledge, currently there are not broad competitive communities or branches of research that have structured themselves around alternative concepts, principles, practices and research programmes (as also shown by the evolution of the use of the different environmental conscious terms in Figure 1 in the Appendix). As a consequence, it is not possible to clearly identify and empirically study different and potentially competitive approaches (e.g., we do have at our disposal enough materials, such as handbooks, journals etc., to clearly identify and analyse the scientific knowledge generated outside GC). Even if GC is not the unique concept that populates sustainability research in chemistry, it is at the moment the most important one, and the only one that refers to both a specific vision on how to move toward a more sustainable chemistry (e.g., the handbook by Anastas and Warner) and to a list of rules that allow to implement such a vision (e.g., the 12 principles of GC). Therefore, we believe that concept of GC, and the corresponding epistemic community, can represent a first important step in order to delineate, and shed light on, an emerging and still fluid field.

3. Data and Methods

To capture the scientific knowledge generated by the GC community, we built a dataset of scientific publications extracted up to 2010 from the ISI Web of Science (WoS). The dataset has been assembled in the following way.

We started by taking into account all papers (i.e., scientific articles and reviews) published in the *Green Chemistry Journal* (GCJ), which, as we have seen in section 2, is one of the main institutional arrangements of the GC community and an important instrument used by the community to make visible its research. The GCJ invites submissions on all aspects of research and policy relating to the endeavour of reducing “*the environmental impact of the chemical enterprise by developing a technology base that is inherently non-toxic to living things and the environment*”⁶ and its scope is explicitly based on the GC vision proposed by Anastas and Warner [2]: “*The scope of Green Chemistry is based on, but not limited to, the definition proposed by Anastas and Warner (Green Chemistry: Theory and Practice, P. T. Anastas and J. C. Warner, Oxford University Press, Oxford, 1998): Green chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products*”⁷. Therefore, we believe that papers published in the GCJ can be considered as a first good indicator of the scientific knowledge generated by the GC community.

However, not all scientific achievements of this community are necessarily published in the GCJ. In order to capture this knowledge, we consider that the language used by the GC community matters and must be taken into account. In particular, we argue that the use of the term “green chemistry” claims for belonging to the community and being acknowledged as a member of the community. As a matter of fact, our interviews with chemists, as well as our participation to focus groups, gave us the opportunity to observe that the use of the expression “green chemistry” is far from being neutral. Most of the chemists that we interviewed prefer to use alternative expressions (e.g., sustainable chemistry, bio-based chemistry etc.) and their explanation for this preference is often linked to their critical view of the GC vision proposed by Anastas and Warner [2]. In particular, they believe that, in such vision, economic considerations and industrial interests have too much weight at the expense of purely scientific ones. Although we cannot exclude cases of improper use of the term, we can claim that research broadly referring to the GC philosophy developed within the EPA tends to use the term “green chemistry” instead of other expressions. In other words, while the other terms used to qualify sustainability research in chemistry are not well defined and are not stabilized, we believe that the term “green chemistry” refers in a sufficiently accurate way to the vision developed within the EPA, as also the results of our empirical analysis seem to confirm. Therefore, we have included in our dataset also all papers using the term “green chemistry” in their titles, abstracts or keywords. We obtained a

⁶ <http://www.rsc.org/publishing/journals/GC/about.asp>, retrieved on 04/04/2012

⁷ <http://www.rsc.org/publishing/journals/GC/about.asp>, retrieved on 04/04/2012

final dataset of 3,832 papers, which, we believe, represent a good, although not perfect indicator of the scientific knowledge generated by the GC community.

To analyze the scientific knowledge generated by the GC community, we used two algorithms for the analysis of citation networks. Analysis is performed on backward citation data associated with the 3,832 papers contained in our GC dataset. We created a network of citations among GC publications, so that papers generated by the GC community correspond to the vertices of a network and are connected with each other by a number of arcs, which symbolize citational links among papers. Each paper represents a discrete piece of scientific knowledge that has passed the scrutiny of the scientific community through the peers review process. Each cited paper represents a previously existing piece of knowledge that has been incorporated and further developed by the citing papers. Citations among papers, making explicit the epistemic links among the pieces of knowledge from which the GC community emerged and grew, can be used to map the dynamics of scientific knowledge. To that purpose, we applied to the network of GC publications the following algorithms implemented by *Pajek*, a freely available software for the analysis and visualization of citation networks.

The first algorithm, the Hubs and Authorities, selects the most prominent vertices of a citation network. Hubs and Authorities are formal notions of structural prominence of vertices [17] and therefore are here used for identifying the contributions that laid the foundations of the GC community (Authorities) and their most important developments (Hubs). The concept at the basis of this algorithm can be dated back to Pinski and Narin [18], who proposed to measure the prominence of scientific journals by taking into account not simply the number of citations that a journal receives, but also the prestige (in terms of citations received) of the journals that cite it [19]. Journals that receive many citations from prestigious journals are considered highly prestigious themselves and, by iteratively passing prestige from one journal to another, a stable solution is reached which reflects the relative prestige of journals [20]. This way of measuring prestige is the basis of the algorithms for evaluating the status of web pages developed by Brin and Page [21] and Kleinberg [22]. Such algorithms have been later adapted by Batagelj [23] for the software *Pajek*⁸. Hubs and authorities stand in a mutually reinforcing relationship: a good authority is a paper that is cited by many good hubs, and a good hub is a paper citing many good authorities [23].

The second algorithm is the Main Path (MP) and selects the most important stream of growth of a citation network. By computing the total number of paths linking the oldest vertices in a citation network to the most recent ones, this algorithm maps all possible streams of cumulative growth of knowledge and identifies the most important one. Therefore, the contributions selected by this algorithm are expected to capture the main scientific trajectory that emerged over the whole evolution of the GC community, since its origin. The MP algorithm is based on the Search Path Count (SPC)

⁸ See [23] for a formal explanation of that algorithm.

method [23]⁹, which calculates traversal weights on arcs following the Hummon and Doreian [24] main path analysis. Traversal weights measure the importance of paths linking entry vertices (i.e., vertices that are not cited within the data set) to exit vertices (i.e., vertices that are not citing within the data set) in a network¹⁰. The MP is the path from entry vertices to exit vertices with the largest traversal weights on its arcs.

The MP algorithm has been used by recent studies on both scientific publications and patent data in order to identify the main technological or scientific trajectories that have characterized the evolution of specific fields (see for example [25-32]). The novelty of our approach compared to those studies is threefold. First, we take as our unit of analysis a whole epistemic community, rather than a relatively narrow and/or established field. This allows us to map, for the first time, the scientific knowledge underlying the evolution of a new epistemic community, and, by doing that, to shed light on a broader emerging area of research that has never been examined before using quantitative methods. By reviewing the historical and specialized literature on this emerging field and interacting with the community of practitioners, we have been able to delineate the boundaries of the field through the concept of epistemic community and have built an original dataset of publications by combining papers published in procedural authority of the community (the GCJ) and papers selected through the keywords search of the term used by the members of the community to qualify their research. Second, rather than focusing on one main algorithm of network analysis (the MP algorithm), we have combined two different algorithms (the Main Path algorithm and the Hub and Authorities algorithm). This allows us to identify different dimensions of the relevant knowledge (not only the main scientific trajectory of the GC community, but also the knowledge that laid the foundations of the community) and better grasp the dynamics of knowledge and organizations. Third, we go beyond the analysis of scientific/technological evolution and, by analyzing the scientific knowledge selected by the different network analysis algorithms, we discuss the factors that have shaped the emergence and evolution of a new community of practitioners. To the best of our knowledge, this has never been done in the literature.

There are obvious limitations in using bibliometric data as measure of knowledge dynamics since differences exist across countries, disciplines, authors and organizations in the propensity to publish and cite. However, these data remain the best standardized proxy by which we can account for the overall evolution of knowledge systems and, most importantly, they are defined by the research community itself and not by the analyst [25]. With respect to the communities that are relevant for this

⁹ See [23] for a formal explanation of that method.

¹⁰ Traversal weights on arcs are calculated in the following way. In an acyclic network there is at least one entry vertex and at least one exit vertex. Let us denote with I and O the set of all entries and all exits, respectively. The SPC method assigns to each arc as its weight the number of the different I - O paths passing through the arc. This number is then divided by the total number of paths between entry and exit vertices in the network. This proportion is the traversal weight of an arc.

analysis, papers are a sufficiently reliable indicator of the state of knowledge because in the chemical field the propensity to publish is relatively high [33].

4. Results

In this section, we first show the main trends emerging from the analysis of the GC dataset, highlighting how GC knowledge evolved over time and spread among different scientific journals, disciplines and countries (section 4.1.). We then present the network analysis results, illustrating and discussing the knowledge that laid the foundation of the GC community (section 4.2.) and the main scientific trajectory underlying its whole development (section 4.3.), as well as the countries and organizations involved in generation of the relevant knowledge.

4.1. Evolution and distribution of GC knowledge

Figure 1 displays the distribution of GC publications over the last three decades and shows the exponential growth of the GC community since 1999, just after the publication of the GC handbook with the 12 Principles of GC (1998) and the creation of the GCJ (1999). Thus, following the premises of GC such as launched by the EPA during the period 1993-1998, the GC community has gained ground with the codebook and the procedural authority that have made possible the diffusion of a common vision and the generation of new scientific knowledge. The growth of GC knowledge has been particularly important in 2002 and in 2009, when GC publications almost doubled.

Insert Figure 1 about here

Table 1 shows the top 10 Scientific Journals where the GC community published its achievements. The GCJ hosts almost half of GC publications, while among the other top journals, we find some of the highest ranked and generalist journals in the chemical field, including *Tetrahedron*, *Chemistry - A European Journal* and *Angewandte Chemie*. These results show that the scientific knowledge generated by the GC community is highly concentrated in the GCJ (the procedural authority), but they also suggest that GC research has obtained a good visibility within the broader chemical community.

Insert Table 1 about here

By examining the main subject areas of GC publications, contained in Table 2, we observe that most of GC papers belong to field *Multidisciplinary Chemistry* (63.36%). This result accounts for the

diversity of disciplinary approaches that characterizes GC research, which is also emphasized in the GC vision proposed by Anastas and Warner [2]. This multidisciplinary approach is reflected as well – though in a lesser extent – by the presence of the subject area *Environmental Sciences*, an interdisciplinary academic field that integrates physical and biological sciences for the solution of environmental problems. If we consider the other top subject areas of GC publications, we observe that besides more traditional fields (i.e., *Organic Chemistry*, *Physical Chemistry*, *Inorganic & Nuclear Chemistry*), also applied fields, including *Applied Chemistry*, *Chemical engineering*, *Polymer science*, *Applied Microbiology & Biotechnology*, play a significant role. This seems to suggest that applied research an important part of GC.

Insert Table 2 about here

Finally, table 3 shows the distribution of GC publications among the top 20 countries. The United States come first, with 18.14% of total GC papers, showing their persistent leadership in the generation of GC knowledge. However, data also highlight that emerging countries are playing an increasing important role in the community, especially China, which is challenging the US leadership with a share of 15.34% out of all GC papers. India accounts for 8.09% of total GC papers, just behind Japan (8.77%). European countries, especially England, France, Germany, Spain and Italy, appear to be key players as well in GC research: the total share of European countries ranked among the top 20 countries amounts to 39.8% of total GC publications. These results show that even if the GC community has emerged in the US, it has spread over a wide range of countries, including emerging countries. This also suggests that the development and consolidation of the chemical industry in these emerging countries goes with the integration of sustainability goals, at least in the scientific sphere. In China for example, there are more than a dozen universities with key laboratories in GC that are supported at national and provincial levels (see also [34]). The key role played by European countries in GC research also coincides with a strong policy support at the level of the European Community. Such a support has also been given through The European Technology Platform for Sustainable Chemistry (SusChem)¹¹, which has actively encouraged chemical R&D in Europe and in 2008 has given birth to a new scientific journal, *ChemSusChem* explicitly aimed at advancing sustainable chemistry. Political support for the development of GC has been given in Japan as well, through a variety of initiatives (see for example [6]).

Insert Table 3 about here

¹¹ <http://www.suschem.org/>. It is still not clear what the differences are between the vision underlying SusChem and the GC vision referring to the US EPA. That issue will be object of further research

4.2. Foundations of the GC Community

Tables 4 and 5 display, respectively, the top 10 Authoritative and Hub papers, which represent the contributions that laid the foundations of the GC community (Authorities) and their most important developments (Hubs). A first look at these papers shows that authoritative papers were mainly generated by US and UK organizations in the early 2000s, following the publication of the 12 Principles of GC, while Hub papers were developed in the late 2000s by organizations based in Japan, China, and Iran. This reveals that while the GC foundations were largely laid by the US-UK community, the main developers of this fundamental knowledge are Asian countries.

Insert Table 4 and 5 about here

If we now go deeper in the analysis of Hub and Authoritative papers, we first get the confirmation that the foundations of the GC community were primarily laid by the "Fathers of Green Chemistry", altogether with the network of institutions launched by the EPA. Indeed, among the top 10 authoritative papers, we found 4 contributions concerned with the main achievements, challenges and opportunities of GC¹². The authors of these papers are Prof. Paul Anastas (Assistant Administrator for EPA's Office of R&D), Prof. James Clark (founding director of the GC Network and founding Scientific Editor for the GCJ) and Prof. Martyn Poliakoff (Chair of the Editorial Board of the GCJ). The main organizations involved are the EPA, the University of Nottingham and the University of York. These papers have been published in high ranked and generalist journals, including *Accounts of Chemical Research* and *Science*, as well as in the GCJ. This confirms that the GC approach proposed by the EPA has received a great attention within the broader chemical community. These results also emphasize the capacity of both the procedural authority and the founders of the epistemic community in producing the most prominent pieces of GC knowledge.

As anticipated, such papers strive to expose the GC philosophy and vision. GC is here conceived as an overarching approach applicable to all aspects of chemistry, from feedstocks to solvents, synthesis and processing. Environmental issues are explicitly addressed, emphasizing the importance of GC in promoting an approach to environmental problems that shifts away from the historic "command-and-control" and prioritizes the prevention of pollution at its source. It is important to note that, in these papers, economic considerations are a major argument. Indeed, GC is claimed to seek new technologies that are both cleaner and economically competitive, and the economic benefits of GC are considered as central drivers in its advancement (Authoritative paper *Anastas and al., 2001*). Emphasis is also put on both the identification of potential barriers to the implementation of GC techniques by the industry and the reduction of operating costs associated to the use of GC. Thus, very

¹² These are *Anastas and Kirchhoff (2002)*, *Poliakoff and al. (2002)*, *Clark (1999)*, *Anastas and al. (2001)*

early, the fathers of GC have emphasized the potential win-win effects (in the sense of Porter and van der Linde [35]) of GC innovation and the role of public policy in supporting such eco-innovations.

A second important focus contained in Hub and Authoritative papers relates to alternative catalysis, and, more in particular, the design of environmentally benign, reusable or recyclable catalysts. This topic is indeed addressed by 3 Authoritative papers¹³ – all published in top ranked journals like *Accounts of Chemical Research*, *Angewandte Chemie* and *Chemistry of Materials* – and it is further developed by most of the Hub papers (8 out of 10)¹⁴. Thus, research on alternative catalysis appears to be a fundamental topic of the GC community and, given the importance of the scientific journals where this research has been published, advances in this field are likely to impact on the broader chemical community. Though this topic has been launched by Prof. Clark (i.e., Authoritative paper *Clark (2002)*), from the University of York, it turns that Japanese organizations have come to play a dominant role. Indeed, as we can see from Tables 4 and 5, the main organizations involved in research on alternative catalysts are the *Tokyo Institute of Technology*, the *National Institute of Advanced Industrial Science and Technology*, and the *Kanagawa Academy of Science and Technology*. Despite the Japanese dominance in this area of GC research, the most recent developments on alternative catalysts were generated in two emerging countries, namely China and Iran¹⁵.

In these contributions on alternative catalysis, as in the previous ones, economic considerations and industry interests are explicitly considered. Indeed, all mentioned papers focus on carbon-based solid acids as replacement for sulfuric acid in the chemical synthesis of various compounds. The industry interest on these developments is high since sulfuric acids are one of the most used catalysts (over 15 million tons per year) in the production of industrially important chemicals, but they are not recyclable and requires costly and inefficient separation procedures, resulting in a huge waste of energy and large amounts of waste products. The efforts of these papers are thus devoted to show that carbon-based solid acids, besides being comparable to sulfuric acids for catalytic activity and selectivity, are also stable products, which can be efficiently synthesized, sometimes in one-step, from inexpensive starting materials and used to carry out chemical transformations in fewer steps than conventional processes. Moreover, from a chemical engineering perspective, these catalysts are claimed to be highly desirable because they are readily separable and can be reused or recycled, reducing energy consumption and waste generation.

In the remaining Hub and Authoritative papers, a third important focus arises around the development of a metrics for assessing the potential environmental impact of chemical reactions and processes. This issue is an important challenge for GC since there currently is no all-inclusive

¹³ These are *Clark (2002)*, *Hara et al. (2004)*, and *Okamura et al. (2006)*.

¹⁴ These are *Kitano and al. (2009a)*, *Kitano and al. (2009b)*, *Nakajima and al. (2009)*, *Nakajima and al. (2007)*, *Xiao and al. (2010)*, *Mirkehani and al. (2009)*, *Liang and al. (2007)*, *Shokrolahi and al. (2008)*.

¹⁵ These are Hub papers *Xiao and al. (2010)*, *Mirkehani and al. (2009)*, *Liang and al. (2007)*, and *Shokrolahi (2008)*.

evaluation methodology and the community is discussing a variety of different, competing or complementary, metrics ranging from the concept of “atom economy” to the “E-factor”, and the more recent “reaction mass efficiency” and “carbon efficiency”, mainly used in the pharmaceutical industry. In a broader perspective, metrics and metrology are critical issues for environmental sciences in general, due to the complexity of measuring the environmental performances of new technological processes [36]. As we can see from Tables 4 and 5, this topic is addressed by 2 Authoritative papers (i.e., *Curzons and al. (2001)* and *Constable and al. (2002)*), both published in the GCJ and generated at GlaxoSmithKline, one of the most important worldwide pharmaceutical companies, headquartered in London. The paper by *Curzons and al. (2001)* focuses on the evaluation of process technologies used in the pharmaceutical industry and explicitly adopts a “*corporate perspective*”, while *Constable and al. (2002)* examine the “*reaction mass efficiency*” metrics using “*an economic analysis of four commercial pharmaceutical processes to understand the relationship between metrics and the most important cost drivers in these processes*”. These results provide further evidence for the important role played by industry interests and perspectives in the development of GC, even in the knowledge that is supposed to lay the foundation of the community. These results also highlight the interest of pharmaceutical industry in GC advancement, in particular for reducing the costs of pharmaceutical processes. A further development of this topic is represented by the highest ranked Hub paper by *Gonzalez and Smith (2003)*, both from the EPA. This work deals with the development of an indicator model called GREENSCOPE¹⁶ that provides a quantitative definition of process sustainability and can be employed in “*view of the possible implementation of GC technologies on the plant scale*”.

4.3. Main scientific trajectory of the GC community

Figure 2 displays the Main Path (MP), which captures the dominant direction of knowledge accumulation that emerged along the whole evolution of the GC community, i.e., the main scientific trajectory of the GC community. Starting from the bottom of the figure and moving along the vertical axis, we can analyze the content of the papers that form this trajectory and detail its development over time. A first look at these papers reveals that the main scientific trajectory of the GC community has focused on searching alternative solutions to traditional solvents¹⁷. Solvents represent the bulk of reactions’ waste and are heavily used in industrial processes for the isolation, separation and purification of materials, but they are typically toxic, flammable and corrosive. Though the best solvent is no solvent and, as illustrated in section 2.2, there is a variety of alternative solvents that are currently being explored (e.g., supercritical fluids, water, ionic liquids, etc.), the MP shows that, among all possible alternative solvents or no-solvent solutions, ionic liquids (ILs) have very quickly concentrated the

¹⁶ “*Gauging Reaction Effectiveness for the Environmental Sustainability of Chemistries with a multi-Objective Process Evaluator*”.

¹⁷ Detailed information on MP papers are contained in Table 6.

attention of the GC community as replacement of conventional organic solvents. The use of conventional organic solvents leads to VOCs (*Volatile Organic Compounds*) emissions, which are responsible for a large part of the environmental problems of processes in the chemical industry and have a great impact on cost, safety and health (paper LOZANO_P(2010)).

Insert Figure 2 about here

The industry interest in replacing conventional organic solvents is high, since it would allow firms to decrease or eliminate the costs of complying with regulation on VOCs. VOCs emissions are heavily regulated in many countries, including US, where different federal and state legislations exist, Japan with the Air Pollution Control Law, and Europe with the Directive 1999/13/CE, which not only regulates VOCs emissions, but also encourages firms to develop new clean technologies for reducing VOCs emissions at their source [37]. Indeed, as we can see by reading MP papers, a major reason behind the great interest showed by the GC community in ILs as alternative solvents is their negligible vapor pressure, which causes reduced air emission (see for example papers DOCHETRY_K(2005), STOLTE_S(2008)). Moreover, the specific physico-chemical properties of ILs are claimed to make them suitable for numerous industrial applications in different fields like organic synthesis, catalysis, biocatalysis, and electro-chemistry. Such properties, which include thermal and electrochemical stability, high conductivity and high ability to dissolve a wide range of compounds, can be also modified and optimized for a defined technical application (paper STOLTE_S(2008)). These advantages also help explaining why ILs have represented an attractive focal point in the GC community.

If we now look more closely at the MP, such as depicted by figure 2, we can detail the evolution over time of the GC community, while building new knowledge on ILs as alternative solvents. We identified 5 stages of development. The first stage, which represents the early days of the GC community (i.e., papers in the bottom layer of the figure), consists in the exploration of different alternative solvents or solvent-free reactions. In particular, KITAZUME_T(1999) proposes a no-solvent approach to enzymatic reactions, while NAKANO_H(1999a, 1999b) analyzes the utility of fluororous liquids as alternative solvents for important reactions used in industrial production (i.e., Lewis acid catalyzed reactions and Friedel–Crafts reactions). The paper EARLE_M(1999) is particularly important, since it proposes to use ILs as alternative recyclable solvents in a widely used reaction in the chemical industry (i.e., the Diels–Alder reaction), envisaging the possible employment of ILs on an industrial scale. Among the authors of this paper, we find Prof. Kenneth Seddon, one of the “fathers” of ILs. All the contributions of this first stage of development were published in the first volume of the GCJ.

In the second stage, and following the paper EARLE_M(1999), ILs already attract the interest of the community. Indeed, during this period (papers from KITAZUME_T(2000) to DOMANSKA_U(2003)), GC research is devoted to show the utility of ILs as green solvents for various reactions and to synthesize new ILs with better physico-chemical properties in order to favor their applications to new industrial processes. The paper DOMANSKA_U(2003), published in *Chemistry – A European Journal* and generated at the *Warsaw University of Technology*, illustrates particularly well the influence of environmental regulation on the selection of ILs as alternative solvents. The paper indeed explicitly refers to the clean technology approach underlying the European Directive on VOCs mentioned above (i.e., Directive 1999/13/CE) and it points to the use of ILs solvents as “*one of the main strategies of clean industrial technology*”.

The focus on ILs continues in the third phase, going from 2004 to 2007, when the GC community concentrates on assessing the potential environmental impact of ILs, in view of their widespread use in the industry and consequent release in the environment (paper (DOCHERTY_K(2005))). However, it appears that the keen interest first granted to ILs has left room to uncertainties and controversies. Indeed, the general lack of knowledge surrounding the environmental impact of ILs is viewed by the community as a major impediment to the adoption of these compounds by industry (paper COULING_D(2006)). Consequently, papers published during this period (i.e., papers from SWATLOSK_R(2004) to STOLTE_S(2007b)) propose different methods and experiments for assessing ILs toxicity with the aim of contributing to the design of less toxic ILs. SWATLOSK_R(2004) claims that the growing attention on ILs as new solvents within the GC community has outstripped the environmental and toxicological data available and he proposes a model (i.e., the *Caenorhabditis elegans*) for exploring the toxicological effects of ILs. Interestingly, papers STOLTE_S(2007a) and STOLTE_S(2007b) also stress the increasing importance of understanding the (eco)toxicological hazard of ILs in order to avoid the costs associated to the possibility for a chemical product to fail the authorization process envisaged by REACH. These papers emphasize as well the importance of university–industry partnerships in order to combine the (eco)toxicological studies developed in academia with the knowledge on industrial products and processes.

In the fourth phase, the GC community shifts the focus on examining the biodegradability properties of ILs, with the aim of synthesizing ILs that are more biodegradable and therefore that have a reduced environmental impact. In particular, STOLTE_S(2008) and HARJANI_J(2009) stress the importance of the GC principle stating that “*chemicals should also be designed to break down to innocuous substances after their use so that they do not accumulate in the environment*”, proposing new methods for assessing IL biodegradability. Likewise, MORRISSE_S(2009) points out that the contribution of ILs to anthropogenic waste is a major factor hindering their valid classification as green solvents and proposes to synthesize a series of ILs with improved biodegradability properties.

The fifth phase of development reflects the most recent evolution of the GC community. We see that research in this period turned towards the exploration of a wider variety of alternative solvents for use in the field of biocatalysis. Biocatalysis deals with the use of enzymes as alternative and natural catalysts for various reactions, the so-called enzymatic reactions¹⁸. Enzymes perform their catalytic activity using water as solvent, while here their behavior in other alternative solvents is investigated with the aim of improving the catalytic properties of enzymes. In particular, paper LOZANO_P(2010a) considers enzymes as the most powerful green tool for catalyzing chemical processes and it reviews enzymatic reactions in four alternative non-aqueous solvents that are “*the main targets of current academic and industrial research for applied biocatalysis*” (these solvents are: ionic liquids, supercritical fluids, fluorinated solvents and liquid polymers)¹⁹. Thus, it appears from the analysis of these recent developments that the GC community broadened its research focus and is trying to work at the intersection of different knowledge fields or GC principles (i.e., alternative catalysts in alternative solvents). As we can read in one recent review of GC research, this is indeed one of the most important challenges of the GC community: “*The powerful reality that is beginning to be realized and that must be exploited in the future is that the Principles of Green Chemistry can be approached as a unified system. Rather than thinking of the principles as isolated parameters to be optimized separately, one can view the principles as a cohesive system with mutually reinforcing components*” [9].

Finally, we note that MP papers were mainly published in the *GCJ* and were generated in great part by universities based in Europe, including the *University of Bremen*, the *University of Murcia*, the *Queen's University of Belfast*, the *University of Nova Lisboa*, and the *Warsaw University of Technology*. Japanese organizations, in particular the *Tokyo Institute of Technology*, also played a role in generating MP papers, especially during the early phase of development. Conversely, the contribution of US organizations was relatively minor and that of emerging countries negligible.

5. Conclusion

This article has investigated the dynamics of scientific knowledge aimed at inventing and developing a more sustainable way of doing chemistry. In order to circumscribe this emerging and still fluid area of research we have used the concept of epistemic community. By reviewing a broad range of secondary sources and interacting with the community of practitioners, we first have showed how an epistemic community around the concept of GC has emerged and materialized, strongly supported by

¹⁸ See also section 2.2 for more details on biocatalysis.

¹⁹ Following this contribution, paper LOZANO_P(2010b) shows how the synergistic combination of both IL and carbon dioxide solvents for enzyme catalysis can lead to greener and highly efficient processes, while paper ABE_Y(2010) designs an optimal IL solvent for carrying out enzymatic reactions using lipases, an enzyme that catalyzes the formation of fats.

the US EPA. The GC community advocates a specific vision and philosophy, illustrated in the handbook by Anastas and Warner [2] and the 12 principle of GC. This handbook and the *Green Chemistry Journal* can be considered, respectively, as the codebook and the procedural authority of the GC community. We are aware that the concept of GC, and the corresponding epistemic community, does not capture the whole scientific knowledge underlying the movement towards a more sustainable chemistry. However, as discussed with more details in section 2, we believe that these concepts can represent a first important step in order to shed light on the phenomenon, given both the importance of the GC community and the absence of broad competitive communities that have structured themselves around alternative concepts, principles and practices.

In order to examine the scientific knowledge generated by the GC community, we built and analyzed an original dataset of scientific publications. The results illustrate that the GC community has grown exponentially since 2000 and has spread among a wide range of countries, with an important contribution of emerging countries like China and India. GC research has obtained a wide visibility in the broader chemical community and tends to use multidisciplinary approach.

By further exploring GC knowledge through citation network methods, we have been able to identify and discuss the foundations of the GC community and its main scientific trajectory. Our analysis emphasizes that the fundamental knowledge of the GC community was importantly shaped by the GC philosophy and vision developed by the "Fathers of Green Chemistry" and the network of institutions launched by the US EPA. In such a vision, economic considerations and industry interests play a major role. We then found that research on alternative catalysts appears to be a fundamental topic of the GC community and advances in this field are likely to impact the broader chemical community. The focus on catalysis seems to be importantly linked to the industry interest regarding those developments because of the potential of the alternative catalysts studied (i.e., carbon-based solid acids) to combine economic and environmental performances. Another fundamental topic of the GC community is the development of a metrics for assessing the potential environmental impact of chemical processes. Here, toxicity and ecotoxicity measurements are at the core of evaluation of process technologies from a corporate perspective and the pharmaceutical industry reveals to play a prominent role. These results suggest that the knowledge that laid the foundations of the GC community is closely linked to policy and industry interests. This, in turn, provides support for the argument according to which this community can be seen as an epistemic community, where the policy receptivity is a crucial issue.

The analysis of the main scientific trajectory that emerged along the whole evolution of the GC community led us to find that the early days of GC have focused on searching alternative solutions to traditional solvents. This trajectory exhibits then a quick focus, within the domain of all possible alternative solvents, on ionic liquids (ILs) as replacement to conventional and highly polluting organic

solvents. It seems that the need for industry to discover new solvents in order to comply with regulation (i.e., regulation on VOCs emission) acted as a "focusing device" in stimulating research on ILs. The most recent evolution of the trajectory shows that GC research broadened its focus (in particular to the field of biocatalysis) and is trying to work at the intersection of different knowledge fields or principles. We also examined the organizations that generated GC knowledge and found that while the foundations of the GC community and their most important developments were mainly laid, respectively, by US and Japanese organizations, European universities were key players in generating the main scientific trajectory of GC.

Overall, these results suggest that policy and industry interests, as well as regulation, have played a significant role in shaping the emergence and evolution of GC. We would also like to note that this article, besides its main contribution, which resides in the thorough analysis of an emergent and important scientific field, also contributes to citation networks studies (see section 3 for more details). In the literature, the network analysis algorithms here employed have been mainly used to identify the technological/scientific trajectories that have characterized the evolution of relatively specific and/or established fields (e.g., [25-32]). Here, we show, for the first time, that those algorithms can also be used to study the emergence and evolution of new epistemic communities, and by doing that, to shed light on broader emerging areas of research. Moreover, we have gone beyond the analysis of scientific/technological evolution and have tried to discuss the factors that have shaped such new communities of practitioners.

To conclude, this study also highlights a new, even though indirect, approach to (eco)innovation policies, which, rather than simply funding scientific research, focuses on supporting the structuring of new communities of practitioners around general but clearly perceived needs (e.g., reducing the human and environmental health consequences of chemical enterprises). Following the premises of GC such as launched by the US EPA, the GC community has gained ground with its codebook and the procedural authority that have made possible the diffusion of a common vision and the generation of new scientific knowledge, which, in turn, has been used to develop more sustainable chemical processes and products.

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Tables and figures

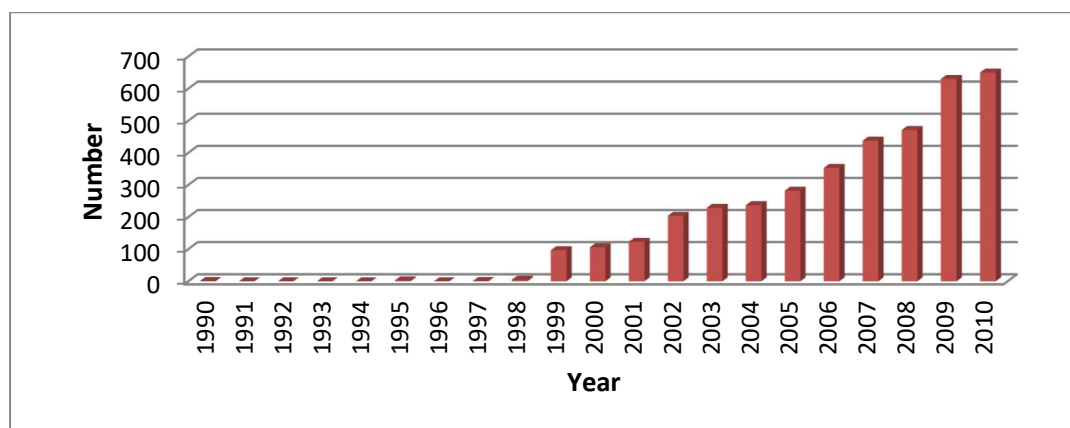


Figure 1. Evolution of GC publications over time

Source: Web of Science

Table 1. Distribution of GC publications among scientific journals

Source: Web of Science

Source Title	% of 3832
GREEN CHEMISTRY	46,63
TETRAHEDRON LETTERS	2,53
CHEMISTRY-A EUROPEAN JOURNAL	2,04
ANGEWANDTE CHEMIE-INTERNATIONAL EDITION	1,96
ADVANCED SYNTHESIS & CATALYSIS	1,93
SYNLETT	1,83
EUROPEAN JOURNAL OF ORGANIC CHEMISTRY	1,15
SYNTHETIC COMMUNICATIONS	1,10
TETRAHEDRON	0,94
SYNTHESIS-STUTT GART	0,81

Table 2. Distribution of GC publications among scientific fields
Source: Web of Science

Subject Area	% of 3832
CHEMISTRY, MULTIDISCIPLINARY	63,36
CHEMISTRY, ORGANIC	16,57
CHEMISTRY, PHYSICAL	6,71
CHEMISTRY, APPLIED	4,28
ENGINEERING, CHEMICAL	3,71
ENVIRONMENTAL SCIENCES	2,35
POLYMER SCIENCE	2,35
BIOTECHNOLOGY & APPLIED MICROBIOLOGY	2,32
CHEMISTRY, INORGANIC & NUCLEAR	1,98
MATERIALS SCIENCE, MULTIDISCIPLINARY	1,96

Table 3. Distribution of GC publications among countries
Source: Web of Science²⁰

Country/Territory	% of 3832
USA	18,14
PEOPLES R CHINA	15,34
JAPAN	8,77
INDIA	8,09
ENGLAND	7,83
FRANCE	6,24
GERMANY	5,82
SPAIN	5,30
ITALY	5,04
IRAN	3,31
BRAZIL	3,08
CANADA	2,48
AUSTRALIA	2,45
NETHERLANDS	2,24
PORTUGAL	1,49
POLAND	1,46
SWITZERLAND	1,33
NORTH IRELAND	1,25
SWEDEN	0,91
BELGIUM	0,89

²⁰ Country counts are based on the institutional affiliations given on published papers. A paper is attributed to a country/territory if the paper carries at least one address from that country/territory. All addresses are considered, not only the address listed first. If a country/territory appears more than once on a paper, the paper is counted only once for that country/territory. All unique countries/territories on a paper are credited equally for the paper.

Table 4. Authoritative Papers

Authors	Year	Title	Source Title	Author Address
Anastas, PT Kirchhoff, MM	2002	Origins, current status, and future challenges of green chemistry	ACCOUNTS OF CHEMICAL RESEARCH	White House Off Sci & Technol Policy, Washington, DC 20502 USA. Univ Nottingham, Dept Chem, Nottingham NG7 2RD, England. Amer Chem Soc, Green Chem Inst, Washington, DC 20036 US.
Clark, JH	2002	Solid acids for green chemistry	ACCOUNTS OF CHEMICAL RESEARCH	Univ York, Clean Technol Ctr, Green Chem Grp, York YO10 5DD, N Yorkshire, England.
Hara, M Yoshida, T Takagaki, A Takata, T Kondo, JN Hayashi, S Domen, K	2004	A carbon material as a strong protonic acid	ANGEWANDTE CHEMIE-INTERNATIONAL EDITION	Tokyo Inst Technol, Chem Resources Lab, Midori Ku, Yokohama, Kanagawa 2268503, Japan. Japan Sci & Technol Co, CREST, Kawaguchi, Saitama 3320012, Japan. Natl Inst AIST, Inst Mat & Chem Proc, Tsukuba, Ibaraki 3058565, Japan.
Poliakoff, M Fitzpatrick, JM Farren, TR Anastas, PT	2002	Green chemistry: Science and politics of change	SCIENCE	Univ Nottingham, Sch Chem, Nottingham NG7 2RD, England. Rohm & Haas Co, Philadelphia, PA 19106 USA.
Clark, JH	1999	Green Chemistry: challenges and opportunities	GREEN CHEMISTRY	Univ York, Dept Chem, York YO1 5DD, N Yorkshire, England.
Curzons, AD Constable, DJC Mortimer, DN Cunningham, VL	2001	So you think your process is green, how do you know? Using principles of sustainability to determine what is green - a corporate perspective	GREEN CHEMISTRY	GlaxoSmithKline, Worthing BN14 8NQ, W Sussex, England. GlaxoSmithKline, King Of Prussia, PA 19406 USA.
Varma, RS	1999	Solvent-free organic syntheses - using supported reagents and microwave irradiation	GREEN CHEMISTRY	Sam Houston State Univ, Dept Chem, Huntsville, TX 77341 USA. Sam Houston State Univ, Texas Res Inst Environm Studies, Huntsville, TX 77341 USA.
Constable, DJC Curzons, AD Cunningham, VL	2002	Metrics to 'green' chemistry - which are the best?	GREEN CHEMISTRY	GlaxoSmithKline Pharmaceut, King Of Prussia, PA 19406 USA. GlaxoSmithKline Pharmaceut, Worthing BN14 8NQ, W Sussex, England.
Okamura, M Takagaki, A Toda, M Kondo, JN Domen, K Tatsumi, T Hara, M Hayashi, S	2006	Acid-catalyzed reactions on flexible polycyclic aromatic carbon in amorphous carbon	CHEMISTRY OF MATERIALS	Tokyo Inst Technol, Chem Res Lab, Midori Ku, Yokohama, Kanagawa 2268503, Japan. Natl Inst Adv Ind Sci & Technol, Res Inst Instrumentat Frontier, AIST, Tsukuba, Ibaraki 3058565, Japan. Univ Tokyo, Sch Engn, Dept Chem Syst Engn, Bunkyo Ku, Tokyo 1138656, Japan. Japan Sci & Technol Co, SORST, JST, Taito Ku, Tokyo 1100015, Japan.
Anastas, PT Kirchhoff, MM Williamson, TC	2001	Catalysis as a foundational pillar of green chemistry	APPLIED CATALYSIS A-GENERAL	Univ Nottingham, Dept Chem, White House Off Sci & Technol Policy, Nottingham NG7 2RD, England. US EPA, Washington, DC 20460 USA. Trinity Coll, Washington, DC USA.

Table 5. Hub Papers

Authors	Year	Title	Source Title	Author Address
Gonzalez, MA Smith, RL	2003	A methodology to evaluate process sustainability	ENVIRONMENTAL PROGRESS	US EPA, Off Res & Dev, Natl Risk Management Res Lab, Cincinnati, OH 45268 USA.
Kitano, M Arai, K Kodama, A Kousaka, T Nakajima, K Hayashi, S Hara, M	2009	Preparation of a Sulfonated Porous Carbon Catalyst with High Specific Surface Area	CATALYSIS LETTERS	Tokyo Inst Technol, Mat & Struct Lab, Midori Ku, Yokohama, Kanagawa 2268503, Japan. Kanagawa Acad Sci & Technol, Takatsu Ku, Kawasaki, Kanagawa 2130012, Japan. Futamura Chem CO LTD, Nakamura Ku, Nagoya, Aichi 4500002, Japan. Natl Inst Adv Ind Sci & Technol, Res Inst Instrumentat Frontier, Tsukuba, Ibaraki 3058565, Japan.
Kitano, M Yamaguchi, D Suganuma, S Nakajima, K Kato, H Hayashi, S Hara, M	2009	Adsorption-Enhanced Hydrolysis of beta-1,4-Glucan on Graphene-Based Amorphous Carbon Bearing SO ₃ H, COOH, and OH Groups	LANGMUIR	Kanagawa Acad Sci & Technol, Takatsu Ku, Kawasaki, Kanagawa 2130012, Japan. Tokyo Inst Technol, Mat & Struct Lab, Midori Ku, Yokohama, Kanagawa 2268503, Japan. Natl Inst Adv Ind Sci & Technol, Res Inst Instrumentat Frontier, Tsukuba, Ibaraki 3058565, Japan.
Nakajima, K Okamura, M Kondo, JN Domen, K Tatsumi, T Hayashi, S Hara, M	2009	Amorphous Carbon Bearing Sulfonic Acid Groups in Mesoporous Silica as a Selective Catalyst	CHEMISTRY OF MATERIALS	Tokyo Inst Technol, Mat & Struct Lab, Midori Ku, Yokohama, Kanagawa 2268503, Japan. Tokyo Inst Technol, Chem Resources Lab, Midori Ku, Yokohama, Kanagawa 2268503, Japan. Natl Inst Adv Ind Sci & Technol, Res Inst Instrumentat Frontier, Tsukuba, Ibaraki 3058565, Japan. Univ Tokyo, Dept Chem Syst Engr, Bunkyo Ku, Tokyo 1138656, Japan. Kanagawa Acad Sci & Technol, Takatsu.
Cai, WQ Cheng, B Zhang, GX Liu, XP	2009	Developing the Green Chemistry Principles	PROGRESS IN CHEMISTRY	Wuhan Univ Technol, Sch Chem Engr, Wuhan 430070, Peoples R China. Wuhan Univ Technol, Sch Mat Sci & Engr, Wuhan 430070, Peoples R China.
Nakajima, K Haraw, M Hayashi, S	2007	Environmentally benign production of chemicals and energy using a carbon-based strong solid acid	JOURNAL OF THE AMERICAN CERAMIC SOCIETY	Tokyo Inst Technol, Mat & Struct Lab, Yokohama, Kanagawa 2268503, Japan. Kanagawa Acad Sci & Technol, Kawasaki, Kanagawa 2130012, Japan. Natl Inst Adv Ind Sci & Technol, Res Inst Instrumentat Frontier, Tsukuba 3058565, Japan.
Xiao, HQ Guo, YX Liang, XZ Qi, CZ	2010	One-step synthesis of a novel carbon-based strong acid catalyst through hydrothermal carbonization	MONATSHFTE FUR CHEMIE	Shaoxing Univ, Inst Appl Chem, Shaoxing, Peoples R China.
Mirkhani, V Moghadam, M Tangestaninejad, S Mohammadpoor-Baltork, I Mahdavi, M	2009	Highly Efficient Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthenes Catalyzed by Carbon-Based Solid Acid Under Solvent-Free Conditions	SYNTHETIC COMMUNICATIONS	Univ Isfahan, Dept Chem, Catalysis Div, Esfahan 8174673441, Iran.
Liang, XZ Gao, S Chen, WP Wang, WJ Yang, JG	2007	Synthesis of a novel carbon based acid catalyst and its catalytic activity for the acetalization and ketalization	CHINESE JOURNAL OF CHEMISTRY	E China Normal Univ, Shanghai Key Lab Green Chem & Chem Proc, Shanghai 200062, Peoples R China.
Shokrolahi, A Zali, A Pouretedal, HR Mahdavi, M	2008	Carbon-based solid acid catalyzed highly efficient oxidations of organic compounds with hydrogen peroxide	CATALYSIS COMMUNICATIONS	Malek Ashtar Univ Technol, Dept Chem, Shahin Shahr, Iran.

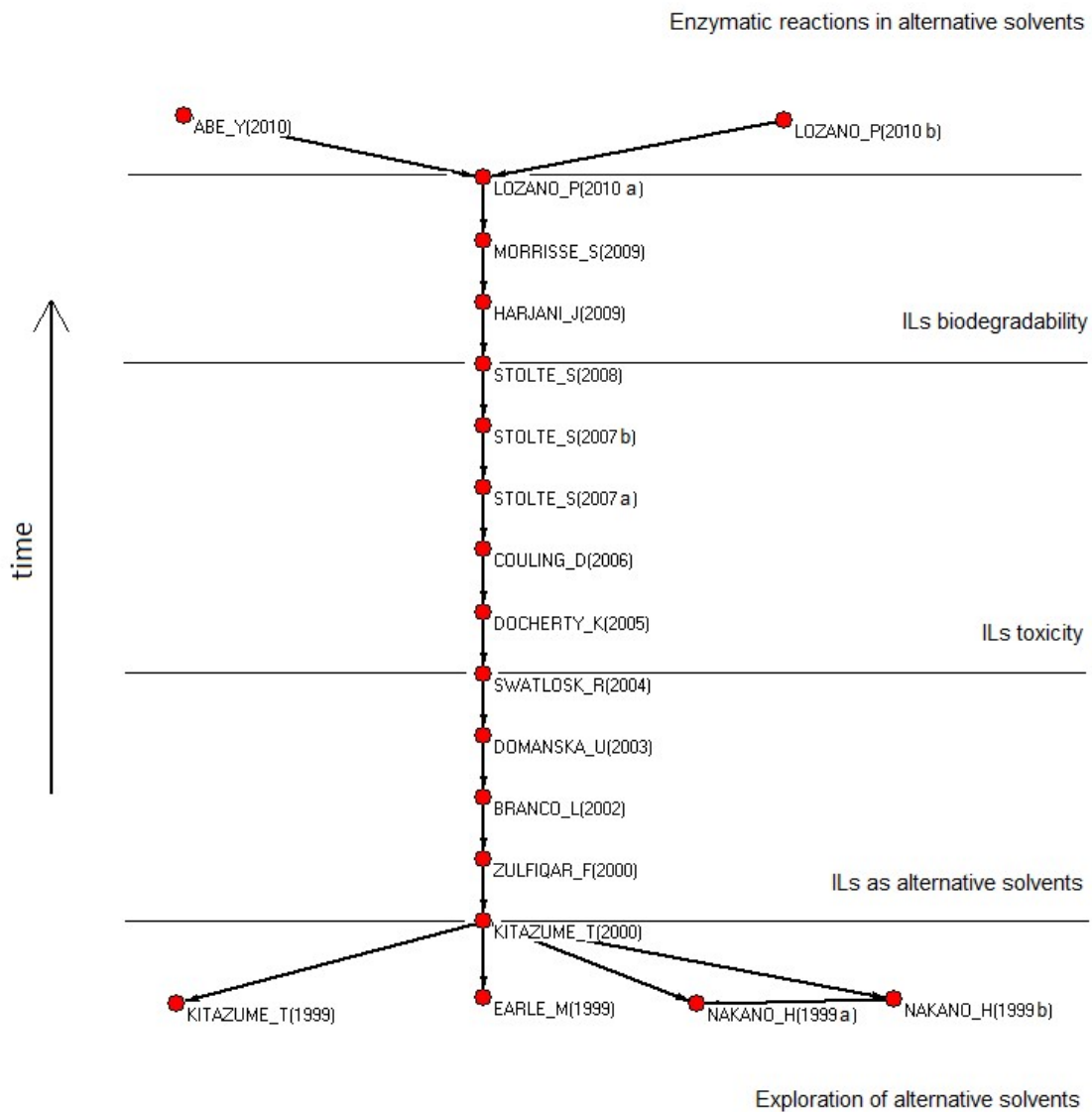


Figure 2. Main Path

Table 6. Main Path Papers

Authors	Year	Title	Source Title	Author Address
Nakano, H Kitazume, T	1999	Organic reactions without an organic medium - Utilization of perfluorotriethylamine as a reaction medium	GREEN CHEMISTRY	Tokyo Inst Technol, Dept Bioengn, Midori Ku, Yokohama, Kanagawa 2268501, Japan.
Kitazume, T Ishizuka, T Takeda, M Itoh, K	1999	A low waste route to large scale enzymatic resolution of a chiral dopant of ferroelectric liquid crystals	GREEN CHEMISTRY	Tokyo Inst Technol, Dept Bioengn, Yokohama, Kanagawa 2268501, Japan. Kashima Oil Co Ltd, R & D Dept, Kashima, Ibaraki, Japan.
Earle, MJ McCormac, B Seddon, KR	1999	Diels-Alder reactions in ionic liquids - A safe recyclable alternative to lithium perchlorate-diethyl ether mixtures	GREEN CHEMISTRY	Queens Univ Belfast, Sch Chem, Belfast BT9 5AG, Antrim, North Ireland.
Nakano, H Kitazume, T	1999	Friedel-Crafts reaction in fluorosolvents	GREEN CHEMISTRY	Tokyo Inst Technol, Dept Bioengn, Midori Ku, Yokohama, Kanagawa 2268501, Japan.
Kitazume, T Zulficar, F Tanaka, G	2000	Molten salts as a reusable medium for the preparation of heterocyclic compounds	GREEN CHEMISTRY	Tokyo Inst Technol, Dept Bioengn, Midori Ku, Yokohama, Kanagawa 2268501, Japan.
Zulficar, F Kitazume, T	2000	Lewis acid-catalysed sequential reaction in ionic liquids	GREEN CHEMISTRY	Tokyo Inst Technol, Dept Bioengn, Midori Ku, Yokohama, Kanagawa 2268501, Japan.
Branco, LC Rosa, JN Ramos, JJM Afonso, CAM	2002	Preparation and characterization of new room temperature ionic liquids	CHEMISTRY-A EUROPEAN JOURNAL	Univ Nova Lisboa, Fac Ciencias & Tecnol, Dept Quim, Ctr Quim Fina & Biotecnol, P-2829516 Caparica, Portugal.
Domanska, U Bogel-Lukasik, E Bogel-Lukasik, R	2003	1-octanol/water partition coefficients of 1-alkyl-3-methylimidazolium chloride	CHEMISTRY-A EUROPEAN JOURNAL	Warsaw Univ Technol, Fac Chem, Div Phys Chem, PL-00664 Warsaw, Poland.
Swatloski, RP Holbrey, JD Memon, SB Caldwell, GA Caldwell, KA Rogers, RD	2004	Using <i>Caenorhabditis elegans</i> to probe toxicity of 1-alkyl-3-methylimidazolium chloride based ionic liquids	CHEMICAL COMMUNICA TIONS	Univ Alabama, Ctr Green Mfg, Tuscaloosa, AL 35487 USA. Univ Alabama, Dept Chem, Tuscaloosa, AL 35487 USA. Univ Alabama, Dept Biol Sci, Tuscaloosa, AL 35487 USA.
Docherty, KM Kulpa, CF	2005	Toxicity and antimicrobial activity of imidazolium and pyridinium ionic liquids	GREEN CHEMISTRY	Univ Notre Dame, Dept Biol Sci, Notre Dame, IN 46556 USA.
Couling, DJ Bernot, RJ Docherty, KM Dixon, JK Maginn, EJ	2006	Assessing the factors responsible for ionic liquid toxicity to aquatic organisms via quantitative structure-property relationship modeling	GREEN CHEMISTRY	Univ Notre Dame, Dept Chem & Biomol Engn, Notre Dame, IN 46556 USA.
Stolte, S Arning, J Bottin-Weber, U Muller, A Pitner, WR Welz-Biermann, U Jastorff, B Ranke, J	2007	Effects of different head groups and functionalised side chains on the cytotoxicity of ionic liquids	GREEN CHEMISTRY	Univ Bremen, Ctr Environm Res & Technol, UFT, D-28359 Bremen, Germany. Merck KGaA, D-64293 Darmstadt, Germany.
Stolte, S Matzke, M Arning, J Boschen, A Pitner, WR Welz-Biermann, U Jastorff, B Ranke, J	2007	Effects of different head groups and functionalised side chains on the aquatic toxicity of ionic liquids	GREEN CHEMISTRY	Univ Bremen, Dept Bioorgan Chem 3, UFT, Ctr Environm Res & Technol, D-28359 Bremen, Germany.
Stolte, S Abdulkarim, S Arning, J	2008	Primary biodegradation of ionic liquid cations, identification of degradation products of 1-	GREEN CHEMISTRY	Univ Bremen, Dept Bioorgan Chem 3, Ctr Environm Res & Technol, UFT, D-28359 Bremen, Germany.

Blomeyer-Nienstedt, AK Bottin-Weber, U Matzke, M Ranke, J Jastorff, B Thoming, J		methyl-3-octylimidazolium chloride and electrochemical wastewater treatment of poorly biodegradable compounds		Univ Bremen, Dept Ecol 10, Ctr Environm Res & Technol, UFT, D-28359 Bremen, Germany. Univ Bremen, Dept Proc Integrated Waste Minimisation 4, Ctr Environm Res & Technol, UFT, D-28359 Bremen, Germany.
Harjani, JR Singer, RD Garcia, MT Scammells, PJ	2009	Biodegradable pyridinium ionic liquids: design, synthesis and evaluation	GREEN CHEMISTRY	Monash Univ, Monash Inst Pharmaceut Sci, Parkville, Vic 3052, Australia. St Marys Univ, Dept Chem, Halifax, NS B3H 3C3, Canada.
Morrissey, S Pegot, B Coleman, D Garcia, MT Ferguson, D Quilty, B Gathergood, N	2009	Biodegradable, non-bactericidal oxygen-functionalised imidazolium esters: A step towards 'greener' ionic liquids	GREEN CHEMISTRY	Dublin City Univ, Sch Chem Sci, Nat Inst Cellular Biotechnol, Dublin 9, Ireland. CSIC, IIQAB, Dept Surfactant Technol, Jordi Girona, Spain. Dublin City Univ, Sch Biotechnol, Nat Inst Cellular Biotechnol, Dublin 9, Ireland.
Lozano, P	2010	Enzymes in neoteric solvents: From one-phase to multiphase systems	GREEN CHEMISTRY	Univ Murcia, Dept Bioquim & Biol Mol & Immunol B, Fac Quim, E-30100 Murcia, Spain.
Lozano, P Garcia-Verdugo, E Karbass, N Montague, K De Diego, T Burguete, MI Luis, SV	2010	Supported Ionic Liquid-Like Phases (SILLPs) for enzymatic processes: Continuous KR and DKR in SILLP-scCO ₂ systems	GREEN CHEMISTRY	Univ Murcia, Dept Bioquim & Biol Mol & Immunol B, Fac Quim, E-30100 Murcia, Spain. Univ Jaume 1, Dept Quim Inorgan & Organ, E-12071 Castellon de La Plana, Spain. CSIC, Inst Catalisis Petroleoquim, E-28049 Madrid, Spain.
Abe, Y Yoshiyama, K Yagi, Y Hayase, S Kawatsura, M Itoh, T	2010	A rational design of phosphonium salt type ionic liquids for ionic liquid coated-lipase catalyzed reaction	GREEN CHEMISTRY	Tottori Univ, Grad Sch Engn, Dept Chem & Biotechnol, Tottori 6808552, Japan.

Appendix

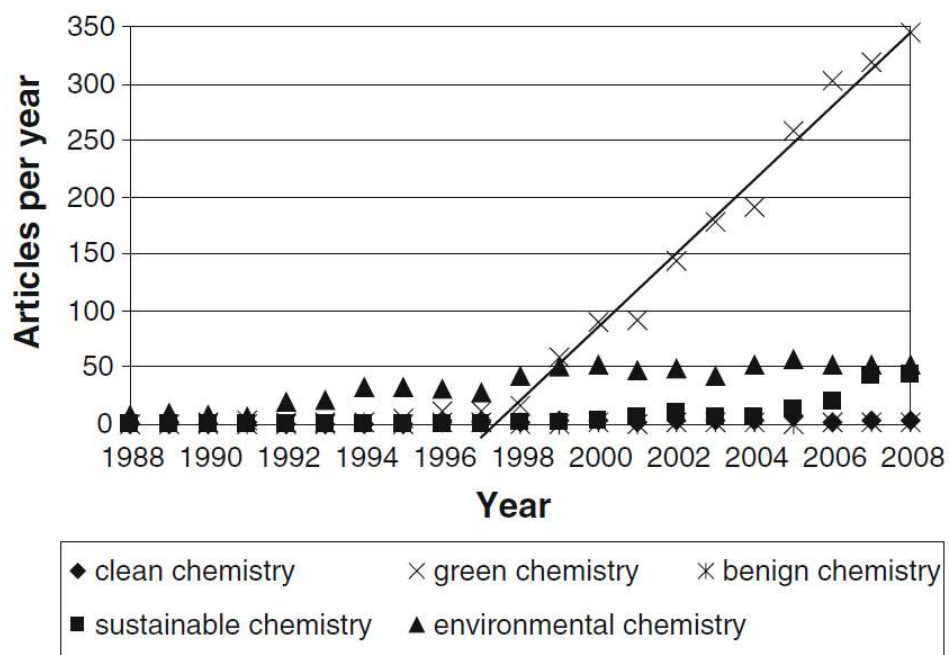


Figure 1. The use of environmentally conscious terms in titles, abstracts and keywords of articles over the 1988-2008 period.
Source: Linthorst (2010)

Table 1. The Twelve Principles of Green Chemistry.
Source: Anastas and Eghbali (2010)

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1. **Prevention.** It is better to prevent waste than to treat or clean up waste after it is formed.
 2. **Atom Economy.** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
 3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.
 4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
 5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
 6. **Design for Energy Efficiency.** Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
 7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
 8. **Reduce Derivatives.** Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
 9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
 10. **Design for Degradation.** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
 11. **Real-Time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
 12. **Inherently Safer Chemistry for Accident Prevention.** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
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