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Prof. Dr. Mustafa Şahin DÜNDAR Editor

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Message from the Editor-in-Chief

TOJSAT welcomes you...

We are happy to inform you that the first issue of TOJSAT has been published.

"The Online Journal of Science and Technology (TOJSAT)" is an online journal for scientists, academics, teachers and educators. TOJSAT promotes the development and dissemination of theoretical knowledge conceptual research and professional knowledge.

So much of contemporary technology is based on the sciences, particularly such disciplines as physics, chemistry, biology, and other sciences that deal with the study, measurement, and understanding of natural phenomena. Learn about the technological advancements and scientific achievements that so greatly influence our lifestyle and impact our lives.

Technologies significantly affect human as well as other animal species' ability to control and adapt to their natural environments. The human species' use of technology began with the conversion of natural resources into simple tools. Technology has affected society and its surroundings in a number of ways. In many societies, technology has helped develop more advanced economies (including today's global economy) and has allowed the rise of a leisure class. Many technological processes produce unwanted by-products, known as pollution, and deplete natural resources, to the detriment of the Earth and its environment.

The Online Journal of Science and Technology (TOJSAT) diffuse the scientific knowledge and researches among academicians and lead to development in academia.

Without the authors TOJSAT would of course have been impossible. I would like to sincerely thank all of authors for sharing their articles.

Thank you...

Prof.Dr. Aytekin İŞMAN Editor in Chief



Message from the Editor

Dear Readers,

Welcome to the first issue of the The Online Science and Technology Journal which covers the all area of Science and Technology. Globally, this century is called as information era and therefore scientific and technological developments will be most important aspects of the papers.

The First International Science and Technology Conference (ISTEC) hold in October 2010 in Famagusta-North Cyprus. The Online Journal of Science and Technology will provide a platform for national and international academics to share their innovative and relevant research efforts.

The journal, which covers all scientific and technological subjects, will be published 4 times a year. Selected papers of the online science and technology conferences will be published in the journal. The main goal of this journal is to be indexed by science citation or social science citation indexes.

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ADVANCED SURFACE WATER QUALITY MONITORING IN THE PROTECTED AREAS OF EASTERN SERBIA

Dejan Vasović University of Nis, Faculty of Occupational Safety djnvasovic@gmail.com

Miomir Stanković University of Nis, Faculty of Occupational Safety miomir.stankovic@gmail.com Milan Gocić, University of Nis, Faculty of Civil Engineering, mgocic@yahoo.com

ABSTRACT: Water is a complex issue embedding different disciplines from biology, chemistry, physics, law, economics, and politics. However, water quality is affected by many other factors. It's very important to have a holistic approach to do a better assessment and management of a catchment. Previous research and evaluation of anthropogenous effects of discharged wastewater conducted in eastern Serbia, clearly indicates a necessity of advanced surface water quality system development. As the starting point of this research, the protected areas within Studena river basin were chosen. Besides theirs importance as protected areas, abovementioned sites are of tremendous significance for regional water supply system. The biggest water supply sources from which city of Niš is supplied with drinking water are located in this area. Those sources consist of three smaller capped springs, with the flow capacity up to 400 l/s. The paper provides an overview of the necessary activities:

- identification of tracking changes indicators of the quality of surface waters in the protected areas,
- establishment of standardized water quality monitoring in the areas, in compliance with the EU directives in this domain,
- realization of interoperability with information systems used by decision makers, as well by institutions involved in the process of water quality control and preservation.

Keywords: surface water quality, monitoring, protected areas

1. INTRODUCTION

The EU Water Framework Directive implementation process (WFD, 2000/60/EC) in Serbia started at the early beginning of 2004. With regard to this fact, basics of sustainable water management must be considered as the analysis of the international legislation and praxis related to it. In accordance with Water Framework Directive, monitoring, assessment process and integral management of surface waters quality should be based on ecoregional approach, meaning both antropological and hydro morphological assessment. Current state of surface waters quality management praxis in the Republic Serbia need to be improved, with regard to future activities. The basis for monitoring redesign and establishment of intercalibration network is provided (in legislative sense). Basic aim of mentioned water monitoring system redesign is to enable efficient, reliable and comparable evaluation of quality status of surface water bodies. Also, it is important to recognize that ecoregional approach allows both better management of transboundary basins and decentralization of institutions in charged.

During the past several years there have been changes in the conception of the environmental monitoring system. The growing public interest in environmental protection and sustainable development calls for a diffusion of information from the surrounding towards all social groups. This leads to a conclusion that strengthening the ties between scientists, managers, and organizations can contribute to a more adequate ecosystem protection management (Branković, Gocić, Stanković, Trajković, & Stanković, 2006). European and American legislators are taking into consideration the indicators of environmental quality, which enable communication with the public in real time, i.e. at the moment of accident; likewise, these indicators enable accident identification. It is also necessary to include media services in environmental management systems. Development of resource management consistently identifies adaptive monitoring of ecosystems as an underdeveloped tool required for protection of the environment, i.e. biodiversity.

Eastern Serbia covers the area of 7 133 square kilometers, with total number of 284 000 inhabitants. Within the region there are two protected areas: The Djerdap National Park (largest in Serbia and one of the largest in the Europe) and Stara Planina Nature Park. It is still not completely explored and hides numerous environmental treasures, lake Canyon of Jerma river which is widely known by its natural beauties – waterfalls, caves and rare flora and fauna. Within Stara Planina Natural Park there are located a few river basins, relatively small in sense of surface that drains, but with significant importance both for biodiversity protection and for human needs. Examples are basins of Temska, Visočica, Jerma, Kutinska, Jelasnička, and Studena river.

2. PREVIOUS RESEARCH ACTIVITIES

Both Serbian Institute for Nature Conservation and Republic Hidrometeorological Service of Serbia monitors the conditions of ecosystem in the protected areas of Eeastern Serbia. In April 2004, the Serbian Institute for Nature Conservation – Niš Office began realization of the project "Improvement of the conditions of management and control of water and environmental resources in the City of Niš – Serbia", financed by the Italian Government via the Italian Ministry of Foreign Affairs. The main



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partner in the project realization was the City of Niš while other partners were five Niš municipalities (Mediana, Palilula, Crveni Krst, Pantelej, and Niška Banja) public communal enterprise Medijana (departments of sanitation and landscaping), public water supply enterprise Naissus, and public forest management enterprise Srbijašume. The project included hydrobiological research of surface water quality in the protected areas of Jelašnička and Sićevačka Gorges (placed within Eastern Serbia, i.e. within Ecoregion No 7 (Eastern Balcan)). In accordance with the Water Framework Directive (European Comission,2003), that research included both physicochemical (thermal and oxygenation conditions, salinity, acidification status) and biological elements (flora and fauna). Another previous research and evaluation of anthropogenous effects of wastewater indicated a necessity to develop monitoring system for surface water quality in the protected areas of Jelašnička and Sićevačka Gorges, i.e. in the Studena river basin (Gocić, Stanković & Stanković, 2006; Trajkovic, Brankovic &Simic, 2006; Branković, Gocić, Stanković, & Stanković, 2006)

2.1. THE STUDENA RIVER BASIN

The Studena river basin is located to the southeast of Niš. The area of the basin covers the surface of about 5,700 hectares, whereas the river itself is 11,553 metres in length. The basin is situated at 433 metres above sea level on average. Over 80% of the basin is wooded land, while the rest of it is covered with arable land or residential areas. Studena river basin is located within the Ecoregion No 7 (Eastern Balcan)). One of the biggest water supply source from which Niš is supplied with drinking water is located on this river. The source consists of three smaller capped springs, located south of the village of Donja Studena, with the capacity between 240 and 400 l s⁻¹. It satisfies one quarter of the total water demand of the City of Niš. The water, with its excellent chemical content, is sent to the city reservoirs after processing, which only includes chlorination. Two parts of the basin are government-protected: the Kunovica Gorge (ca1,560 ha) as a part of the Sićevačka Gorge Nature Park, and the Jelašnička Gorge (116 ha) as a special natural reservation. The banks of the Studena are home to the following villages: Gornja Studena, Donja Studena, Čukljenik, and Jelašnica, with a total population of 2,700. The average age of the residents is ca 43 and an average household owns 0,9 ha of arable land. The working part of the population is mostly employed in industry, so the land is cultivated solely for private purposes and there is no widespread use of pesticides and artificial fertilizers. There is no industrial activity around the basin. The river is exposed to excess waste water, since there is no sewerage in the villages and all waste water is discharged directly into the river. The locality upstream of Gornja Studena village represents a part of the water course that retained almost all of natural characteristics. The locality downstream of Gornja Studena village represent clear evidence of human influence primarily caused by nutrients from agriculture and from wastewater directly discharged from households.

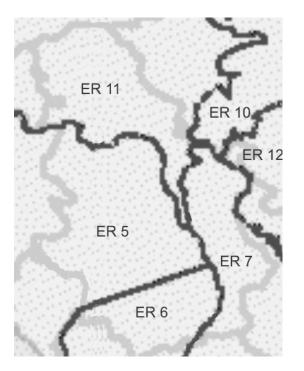


Fig 1: Europe ecoregions for river and lakes – areas in Serbia [4]

2.2. PROJECT OBJECTIVES

Starting from the report by the Serbian Institute for Nature Conservation – Niš Office about environmental quality in the protected areas of Jelašnička and Sićevačka Gorges, and the EU Water Framework Directive (European Comission,2003; European parliament & the council of the european comission,2000), the necessary objectives have been defined. They are based on adequate past and present knowledge and potential future conditions of the ecosystem. Primary objectives:

• identification of parameters for tracking changes in the quality of running waters in the protected areas of Jelašnička and Sićevačka Gorges,

• establishment of a program of long-term standardized measuring and observation of water quality in the areas of Jelašnička and Sićevačka Gorges, in compliance with the EU directives for this domain (European Comission, 2003),

• realization of interoperability with information systems used by decision makers (planners, executives, and managers at the Serbian Institute for Nature Conservation and JKP Naissus), local and regional authorities (Niška Banja Municipality and the City of Niš), as well as by institutions involved in the process of water quality control.

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Specific objectives:

- Synchronization of running water quality monitoring in the protected areas of Jelašnička and Sićevačka Gorges with the EU Water Framework Directive;
- Optimization of the water quality monitoring system by automation of the testing process and selection of indicators and locations for testing;
- Consequent monitoring of quantitative (physicochemical, hydro-biological and microbiological) and qualitative (water flow and water speed) features of fluvial ecosystems in the protected areas of Jelašnička and Sićevačka Gorges;
- Establishment and support to local partner organizations (Institute for Nature Conservation Niš Office, JKP Naissus) in nature protection, to special needs of the population, and to preservation and control of water supply sources;
- Constant monitoring of the water flow ecological values in terms of preservation of ecological status and natural resources;
- Active participation of the general public in the process of informing and consulting on the condition, causes and evaluations of water quality;
- Introduction of e-learning pertaining to running waters.

For the realization of these objectives, the following activities should be considered:

- Analysis of surface water quality;
- Selection of quality parameters and sampling locations;
- Concept of the system for surface water quality monitoring;
- Installation of automated measuring stations;
- Hydro-biological research of surface water quality in the protected areas;
- Monitoring system test phase;
- Reporting to target groups about water quality.



Fig 2: Ecoregion 7; PA – protected area of Stara Planina

2.3. SYSTEM FOR SURFACE WATER QUALITY MONITORING

Actual operational jobs in surface water quality monitoring program are mainly covered by Republic Hydrometeorolological Service that exploits over 200 measuring stations. The majority of those stations (2/3) are of old design, semi-automated. Many analyses are done by daily sampling procedures, requesting additional staff. Simplified scheme of existing surface water quality monitoring system is shown on Figure 3.

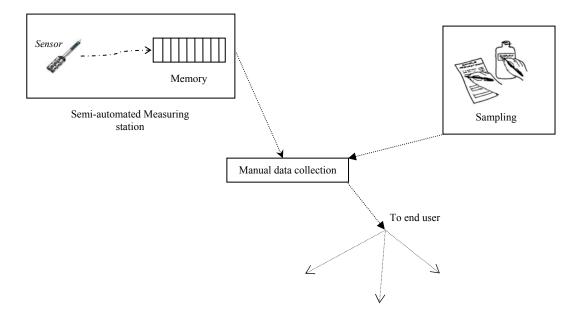


Fig. 3: Surface water quality monitoring system - basic concept

Existing monitoring system could be optimized by partial or complete automation of the testing processes and selection of indicators and locations for testing. Data transfer and reporting procedure are also subjected to possible upgrade to the advanced system for surface water quality monitoring.

3. ADVANCED SYSTEM FOR SURFACE WATER QUALITY MONITORING

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Advanced system for surface water quality monitoring, i.e. monitoring running water quality enables collection, transfer, and modeling of data, and informing target groups on running water quality in the protected areas of Jelašnička and Sićevačka Gorges.

The monitoring system will comprise the following elements:

- Automated measuring stations for measuring water quality parameters,
- Transfer units,
- Appropriate software for communication with the measuring station, for work with the database, for data processing and formation of a model for water quality evaluation, for interoperability with other systems, for creation of reports and visualization of data.

Special attention is given to the development of a module for communication with the measuring station and for interoperability. Data collection would be performed by a measuring station which consists of:

- transmitter-type sensors;
- electronic module for generating trigger impulses of the type 'request for sampling measuring units at a random moment', in order to track sudden quick changes in the measuring parameters;
- electronic module for data storage with battery;
- communication modem;
- solar charge unit.

Connection of remote measuring stations into a unified system is realized by connecting measuring stations into a virtual private network service.

The software will enable the signals, which are read directly from the sensors, and in a format depending on the measuring station type and on the manufacturer, to be formatted in a form suitable for transfer and unique within the whole measuring stations network system. The role of the server software is to receive measuring parameters from measuring stations and automatically create a unifying report in the format required by the Serbian Institute for Nature Conservation for its database. The interoperability module will enable exchange of information with other information systems. This is especially significant in the process of tracking quality parameters of surface waters, considering the fact those institutions which monitor water quality parameters possess their own information systems, and that it is necessary to have access to data from other institutions in order to efficiently make quality decisions within one institution. The interoperability module will be designed in a manner which will completely separate data display from data storage. The system can be dynamically connected to information sources, but it can also dynamically alter the user interface in accordance with user privileges.

In case of unforeseen circumstances, the system will enable asynchronous readouts from individual measuring stations, or summoning of a desired station. Thus, it is possible to obtain measuring from separate measuring stations which might be of interest in a given situation, in irregular order and with a desired reading frequency. A two-way asynchronous communication with individual measuring stations also enables administrators to reconfigure remote measuring stations without any need for physical access to those stations, which may be located in inaccessible areas already covered by the mobile telephony signal. Realization of data transfer from a measuring station to end user is represented in figure 4.



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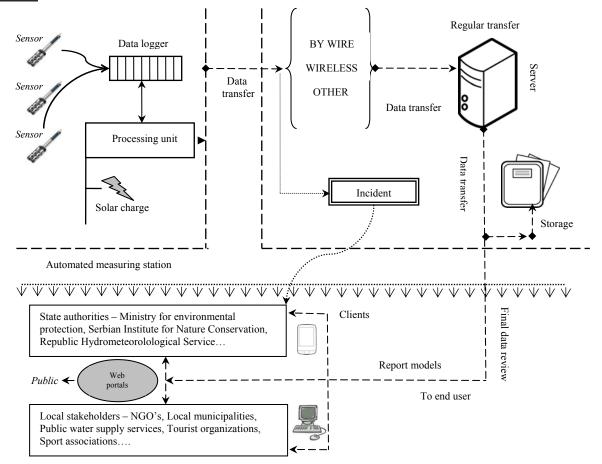


Fig. 4: Advanced system for surface water quality monitoring

4. RECOMMENDED ACTIVITIES

Most water catchment areas in our country are being threatened so fast with pollution due to massive environmental degradation as a result of uncontrolled human activities and unplanned urbanization. This has resulted in increasing cases of water related issues; hence there is need for proper water quality management in order to alleviate this catastrophe. A successful program of ecosystem monitoring enables analysis of both the condition of the ecosystem and the interdependence between this system and social and economic systems. The program of ecosystem monitoring based on the interests of a community (Yarnell Gayton ,2003) is a process with the help of which NGOs and groups of communities or individuals participate in the monitoring of selected types, areas, or processes of an ecosystem. All this is aimed towards upgrading management of ecosystems and natural resources and towards enabling the abovementioned analyses. These analyses represent a basis for developing a system for decision-making support in the management of surface water quality in protected areas. The following activities are being planned:

- integrating the water quality monitoring system into the information system of the Serbian Institute for Nature Conservation,
- developing a module for team work support,
- development of a module to support knowledge-based decision making.

5. CLOSING REMARKS

The paper provides an overview of the activities that should be done in order to improve current surface water quality monitoring system. Starting from previous researches and guidelines for Water Framework Directive implementation, activities have been defined, based on adequate past and present knowledge and potential future states of the ecosystem. Also, the paper evaluates the possible conception of the advanced surface water quality monitoring system. Special attention is given to the development of a module for communication with the measuring station and for interoperability.

Nevertheless, it is particularly important to state that the realization of abovementioned activities would enable the future development of adaptive management of running water quality in the protected areas of Eastern Serbia, which combines local community opinions and defines room for dialogue on the implementation of water preservation strategy.



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INVESTIGATION AND MODELLING OF WATER QUALITY OF GÖKSU RIVER (CLEADNOS) IN AN INTERNATIONAL PROTECTED AREA BY USING GIS

Zeynel Demirel¹, Zafer Özer², Olcay Özer³, ¹Engineering Faculty of Mersin University, Environmental Engineering Department ² Meski, Mersin Municipality zdemirel@mersin.edu.tr,zozer@mersin.edu.tr,olcayozer@mersin.edu.tr

Abstract: Göksu Delta is an important wetland where the Göksu River reaches to sea in the eastern of the town Taşucu-Içel. The delta is classified as a Wetland of International Importance according to the Ramsar Convention on Wetlands of International Importance. The amount of fertilizers used in this area was 7200 tons in 2006. These pollutants affect the surface and groundwater quality negatively. The intensively used fertilizers and pesticides contain not only N- and P compounds but also some heavy metals. The contents of all pollutants in surface waters were determined for four different seasons between 2006 and 2008 and with these data a Geographic Information System (GIS) has been constructed by using Map Info. From the photometric heavy metal analysis, it is inferred that the excess concentration of Fe, Ni, Mn, Mo and Cu at some locations is the cause of undesirable quality for drinking purposes. The source of excess concentration of various heavy metals is the agricultural activities and fertilizers. It is determined that in all periods between 2006 and 2008 the heavy metals and other pollutants, including COD, BOD, NH₃ and NO₃ followed the sharply increasing trends from Silifke city to Mediterranean Sea. The water quality of Göksu River is modeled and determined that the waste water discharge of 10700 m³/day from Silifke city does not create a serious problem because of the high amount of flow rate of Göksu River.

Keywords

Göksu Delta, Göksu River, water pollution, modeling, GIS

1. INTRODUCTION

The Göksu River (Cleadnos) originates in the Taurus Mountains, with a cover area of 10000 km² and total length of nearly 250 km. The Göksu Delta is formed by Goksu River near the Southern part of Silifke town in the Mediterranean region, Turkey. The delta is an important wetland (15000 ha) where the Göksu River reaches to sea in the eastern of the town Tasucu-Ice1 (Ayas et al., 1997). There are two aquatic ecosystems in Göksu Delta; Paradeniz Lake and Akgöl Lagoon. Paradeniz has higher salinity than Akgöl, since it is influenced directly by the exchange of sea water.

Göksu Delta is an internationally important wetland due to its location being on a bird migration route. The Environmental Protection Department of the Ministry of Environment has declared the Goksu Delta as a Special Environmental Protection Zone to protect the area against pollution and exploitation, and to ensure that natural resources and cultural assets have a future. The delta is classified as a Wetland of International Importance according to the Ramsar Convention on Wetlands of International Importance. The Goksu Delta has also a special significance for being one of the few remaining areas in the world where sea turtles (Caretta caretta, Chelonia mydas) and blue crabs (Callinectes sapidus) lay their eggs (Glen et al. 1996; Ayas et al. 1997).

The Mediterranean coastline stretching from the city of Silifke to the Susanoğlu region is heavily populated with recent (last 15 years) urban developments (e.g., villas, apartment complexes, and multi-store buildings), which are mostly occupied during summer season for vacation purposes. Due to an increased population influx from the surrounding cities, especially during the peak season (May to September); the population of this region increases several folds (e.g., 2–4 times). As the urbanization process continues, water pollution problems have become increasingly evident, and have led to serious ecological and environmental problems (Jinzhu Maa et al., 1009) The Göksu Delta is not only an urban area but it is also surrounded by densely cultivated orchards (mostly citrus), traditional vegetable farms and greenhouse cultivations, where farming activities continue all year long



due to favorable climate. The north of the lakes and eastern part of delta consist of farmland where rice, cotton and peanuts are grown all year.

In the Göksu Delta area, urban and agricultural expansions have caused an ever-growing need for fresh water. Population dynamics and agricultural activities in this region have important implications from the surface water chemistry standpoint, especially in the near-shore area, for farmers who rely upon river waters directly for their irrigation. Because the most widespread land use pattern is agriculture in the delta, agricultural inputs caused high levels of contamination within the lagoons of Goksu Delta and river water. Fertilizers and pesticides are used intensively to increase crop yields. Surface water from Göksu River is utilized for irrigation. Most of the irrigation returns flow in the drainage canals discharges back into the Göksu River and transport some pollutant together to this water system. Beside these pollution sources, manure and urban areas with their cesspools are other pollution sources for surface and ground waters in Göksu Delta.

In the previous studies, data showed that about 94 tons of pesticides and 520 kg/ha of mineral fertilizers were used within a year at Göksu Delta (Çetinkaya, 1996). Ayas et al. (1997) reported that various environments and organisms were contaminated by 13 different pesticides and their residues. It was determined that the use of pesticide in Mediterranean region is more than average consumption of Turkey (Dalen et al., 2005). Erdoğan and Karaca (2001) reported that this level was 9.9 kg per ha and 102 different types of pesticides were used in agriculture areas in Göksu Delta. The amount of fertilizers was 7200 tons in 2006. The intensively used fertilizers and pesticides contain not only N- and P compounds but also some heavy metals. These pollutants affect the surface and groundwater quality negatively. The Göksu River has recently been the focus of attention due to recognition of the increasing stress being placed on its water resources and of the resulting environmental degradation in the Göksu delta. Based on surveys and chemical analyses, the surface water qualities in the Göksu Delta were investigated, in order to understand the sources of water pollution and the evolution of water quality in Göksu River.

GIS is an effective tool for storing large volumes of data that can be correlated spatially and retrieved for the spatial analysis and integration to produce the desirable output. GIS has been used by scientists of various disciplines for spatial queries, analysis and integration for the last three decades (Burrough and McDonnell, 1998). The purpose of this study is to understand the pollution of river water with photometric measurements in the basin and modelling and to represent it pictorially using the geographic information system (GIS).

2. Site description

The Göksu Delta is situated in the Mediterranean Sea region of the southeastern part of Turkey and extends from $36^{\circ}15 - 36^{\circ}25$ of latitude north to $33^{\circ}55 - 34^{\circ}05$ of longitude west. The Göksu Delta area is bounded by the Taurus Mountains on the northern side and by the Mediterranean Sea on the southern side. The southern portion of the Göksu Delta area is a delta plain made up of sediments from Göksu River. The Goksu River flow regime is also strongly dependent on the seasonal rains and temperature. Average flow of Goksu River is 130 m³/s where it reaches the highest value during May. Topographic structure in the north of the investigated area (Taurus Mountains) is rugged with altitudes ranging from 300 to 1,500 m.

In the Göksu Delta area, climate is characterized by hot and dry periods in summer and by warm and wet periods in winter, which is typical for the coastal zones around the Mediterranean Sea. The mean annual temperature in this area is 19°C. Showers start in October, and continue till mid April and the maximum rainfall occurs in December. The Göksu Delta area receives slightly higher than 607 mm of precipitation annually, and extended periods (i.e., 3–4 months) without precipitation are common

The geological map obtained from the MTA (General Directorate of Mineral Research and Exploration) is used as the basis for this study. The map was updated and the sampling points were interpreted through digital processing.

The oldest rock unit of the Göksu Delta is Akdere Formation of Paleozoic Age, which consists of marble, schist and quarzite. Akdere Formation (middle-upper devonian) is generally found in the northern part of the study area (Fig. 1). Akdere Formation contains various rocks with differing compositions including sandstone, siltstone, dolomite and limestone. Kusyuvası Formation (Middle trias) consists of limestone. Tokmar Formation (upper jura-lower cretaseous) is found in the western part of delta and contains dolomite and limestone. Tertiary units are composed of oligo-miocene Gildirli formation, lower-middle miocene Karaisali formation and middle-upper miocene Kuzgun formation. (Fig.1). Tertiary rocks consist of a succession of marine, lacustrine, and fluvial deposits, which display transitional characteristics both vertically and areally in the study area.

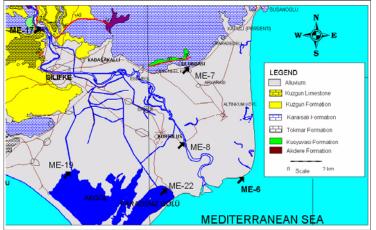


Figure 1. Map showing the water sampling locations and geology of the study area

The Quaternary basin-fill deposits are a heterogeneous mixture of metamorphic and sedimentary rock detritus ranging from clay to boulder size. The mixture includes stream alluvium, stream-terrace deposits, fan deposits, delta deposits, shore deposits. The basin-fill deposits vary greatly in lithology and grain-size, both vertically and areally. Accordingly, the hydraulic properties of these deposits can differ greatly over short distances, both laterally and vertically. The alluvial aquifer consists of a heterogeneous mixture of gravel, sand, silt, clay and sandy-clay. Conceptually the aquifer system in the delta is an unconfined aquifer

3. Materials and methods

For chemical analysis, a total of 6 water samples from the surface waters in Göksu Delta were obtained during 2006-2008 by four separate sampling campaigns at the sampling points shown in Fig. 1. Field work took place between 2006 and 2008, and surface water samples were collected from the Göksu delta. At the same period the contents of all pollutants are determined for four different seasons and with these data a Geographic Information System (GIS) is constructed by using Map Info. Table 1 summarizes the chemical analysis results for water samples collected from the Göksu Delta.

nr	nilligram per	Inter											
			ME-17 (Jöksu			ME-19	Akgöl			ME-22 P	aradeniz	
	Sampling	Ι	II	III	IV	Ι	II	III	IV	Ι	II	III	IV
	period												
	pН	8.02	7.97	8,22	8.4	8.3	8.23	8,6	8.14	8.05	7.98	8.24	8.18
	T (° C)	27.5	27.2	14,3	18.6	33.9	30	11,3	19.1	31	29.1	11.1	22.7
	EC		385	572	568		494		728		48000	33900	35200
	(µS/cm)	335				439		760		45300			
	sal	0	0	0	0	0	0	0,1	0.1	29.6	31.2	20.8	22.1
	DO		6.8		5.77		7.8		3.63		5.4	9.2	8.13
	(mg/L)	7.1		6,32		5.5		8,32		4.9			
	NO_2^-		0	0,06	0		1.31	0	0.03		0.033	0	0
	(mg/L)	0				0				0			
	NO ₃ -		6.9	17,3	8.4		4.6	6,6	9.3		3.6	0	0
	(mg/L)	9.74				6.64				0			
	NH_3		0	0,02	0.012		0	0	0		15.68	0.27	0
	(mg/L)	0.048				0.34				4.01			
	PO_4^{-3}		0	0,28	0.03		0.08	0	0.04		0.3	0.59	0.06
	(mg/L) P ⁵	0.05				0.88				0.39			
			0.1		0.7		1	0	0.2		0.4	0.3	0
	(mg/L)	0.2		0,7		1.4				0.2			
	Br⁻		0.67		0.75		0.52	0,78	0.54		0.43	0.59	0.52
	(mg/L)	0.53				0.72				0.42			

Table 1: Results of chemical analyses of the water samples from four separate sampling campaigns between 2006 and 2008. Concentrations are

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I ⁻ (mg/L) F ⁻	0.4	2.8 0		0 0.26	0.2	0.4 0.42	0,3 0,4	0.3 0.53	3	1.6 1.85	0.7 1.15	1.2 1.2
(mg/L) Na ⁺	0.12	0		0.20	0.83	0.42	0,4	0.55	0.81	1.05	1.15	1.2
(mg/L) K ⁺	5.71				21.7				9556			
(mg/L) Ca ⁺²	1.16				1.86				396			
(mg/L) Mg ⁺²	42.5				36.5				350			
(mg/L) HCO3 ⁻²	17.4				23.8				717			
(mg/L) Cl ⁻	158				213				128			
(mg/L) SO4 ⁻²	10.8				22.5				15177			
(mg/L) KOI	24.4				34.4				2470			
(mg/L) Fe	22	0.0876		0	16	0.49	0,11	0.03	1050	0.94	0.08	0.05
(mg/L) Cu^{+2}	0.64	0.2		0	0.5	1.21	0	0	0.5	0.23	2.81	1.01
(mg/L) Cr^{+6} $(\mu g/L)$	0 0	0		0	0.9 0	0	0	0	0.4 0	0	0	0
Mo^{+6} (mg/L)	0	0		0	0	0	0	0	0	0	0	0
Mn^{+2} (mg/L)	0	0		0	0	0	0	0	0	0	0	0
SiO_2 (mg/L)	5.2	0.087			17.4	5.68	16		7	7.4	25	
	ME (M.	1:4	_			E 7 9				ME	Cilm	
	ME-6 Mee II	diterranear III	n IV	I		E-7 Spr III	ing	IV	I	ME-8 II	Göksu III	IV
	II 7.9	III 8.21	IV 8.12	I 7.65	MI II 7	III 7.4		7.9	I 7.94	II 8.08		8.9
I 7.91 29.2	II 7.9 27	III 8.21 15.3	IV 8.12 20	7.65 22.8	MI II 7 24	III 7.4 19.	7	7.9 21.1	7.94 30.1	II 8.08 26.7	III 8.45 13.9	8.9 18.4
I 7.91 29.2 53500	II 7.9 27 52100	III 8.21 15.3 58000	IV 8.12 20 54000	7.65 22.8 974	MI II 7 24 1016	III 7.4 19. 137	7 72	7.9 21.1 1293	7.94 30.1 1800	II 8.08 26.7 405	III 8.45 13.9 690	8.9 18.4 464
I 7.91 29.2 53500 35.5	II 7.9 27 52100 34.3	III 8.21 15.3 58000 38.1	IV 8.12 20 54000 35.3	7.65 22.8 974 0.3	MI II 7 24 1016 0.3	III 7.4 19. 137 0.5	7 72	7.9 21.1 1293 0.4	7.94 30.1 1800 0.7	II 8.08 26.7 405 0	III 8.45 13.9 690 0.1	8.9 18.4 464 0
I 7.91 29.2 53500 35.5 4.7	II 7.9 27 52100 34.3 4.5	III 8.21 15.3 58000 38.1 8.1	IV 8.12 20 54000 35.3 8.9	7.65 22.8 974 0.3 7.5	MI II 7 24 1016 0.3 5.9	III 7.4 19. 137 0.5 4.4	7 12	7.9 21.1 1293 0.4 5.2	7.94 30.1 1800 0.7 6.4	II 8.08 26.7 405 0 6.4	III 8.45 13.9 690 0.1 6.6	8.9 18.4 464 0 8.4
I 7.91 29.2 53500 35.5 4.7 0	II 7.9 27 52100 34.3 4.5 0.033	III 8.21 15.3 58000 38.1 8.1 0	IV 8.12 20 54000 35.3 8.9 0.03	7.65 22.8 974 0.3 7.5 0	MI II 7 24 1016 0.3 5.9 0.13	III 7.4 19. 137 0.5 4.4 0.0	7 72 3	7.9 21.1 1293 0.4 5.2 0	7.94 30.1 1800 0.7 6.4 0.23	II 8.08 26.7 405 0 6.4 0	III 8.45 13.9 690 0.1 6.6 0	8.9 18.4 464 0 8.4 0
I 7.91 29.2 53500 35.5 4.7 0 6.64	II 7.9 27 52100 34.3 4.5 0.033 2.5	III 8.21 15.3 58000 38.1 8.1 0 0	IV 8.12 20 54000 35.3 8.9 0.03 0	7.65 22.8 974 0.3 7.5 0 17.72	MI II 7 24 1016 0.3 5.9 0.13 2	III 7.4 19. 137 0.5 4.4 0.0 3.5	7 72 3	7.9 21.1 1293 0.4 5.2 0 2.6	7.94 30.1 1800 0.7 6.4 0.23 3.1	II 8.08 26.7 405 0 6.4 0 5.2	III 8.45 13.9 690 0.1 6.6 0 41.2	8.9 18.4 464 0 8.4 0 1.6
I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27	III 8.21 15.3 58000 38.1 8.1 0 0 2	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5	7.65 22.8 974 0.3 7.5 0 17.72 0.17	MI II 7 24 1016 0.3 5.9 0.13 2 0	III 7.4 19. 137 0.5 4.4 0.0 3.5 0	7 72 3	7.9 21.1 1293 0.4 5.2 0 2.6 0	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07	II 8.08 26.7 405 0 6.4 0 5.2 0.02	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32	8.9 18.4 464 0 8.4 0 1.6 0.01
I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01 0.2	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27 0.04	III 8.21 15.3 58000 38.1 8.1 0 0 2 0.14	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5 0.25	7.65 22.8 974 0.3 7.5 0 17.72 0.17 0.06	MI II 7 24 1016 0.3 5.9 0.13 2 0 0.11	III 7.4 19. 137 0.5 4.4 0.0 3.5 0 0.4	7 72 3	7.9 21.1 1293 0.4 5.2 0 2.6 0 0.52	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07 0.27	II 8.08 26.7 405 0 6.4 0 5.2 0.02 0.02	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32 0.58	8.9 18.4 464 0 8.4 0 1.6 0.01 0.51
I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01 0.2 0.7	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27 0.04 0.3	III 8.21 15.3 58000 38.1 8.1 0 0 2 0.14 0.2	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5 0.25 0.2	7.65 22.8 974 0.3 7.5 0 17.72 0.17 0.06 0.5	MI II 7 24 1016 0.3 5.9 0.13 2 0 0.11 0.1	III 7.4 19. 13' 0.5 4.4 0.0 3.5 0 0.4 0.4 0.1	7 72 3 2	7.9 21.1 1293 0.4 5.2 0 2.6 0 0.52 0	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07 0.27 0.6	II 8.08 26.7 405 0 6.4 0 5.2 0.02 0.02 0.6	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32	8.9 18.4 464 0 8.4 0 1.6 0.01 0.51 0
I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01 0.2 0.7 0.58	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27 0.04 0.3 0.55	III 8.21 15.3 58000 38.1 8.1 0 0 2 0.14 0.2 5.37	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5 0.25 0.2 0.52	7.65 22.8 974 0.3 7.5 0 17.72 0.17 0.06 0.5 0.93	MI II 7 24 1016 0.3 5.9 0.13 2 0 0.11 0.1 5.15	III 7.4 19. 135 0.5 4.4 0.0 3.5 0 0.4 0.1 0.5	7 72 3 2 7	7.9 21.1 1293 0.4 5.2 0 2.6 0 0.52 0 0.49	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07 0.27 0.6 0.53	II 8.08 26.7 405 0 6.4 0 5.2 0.02 0.02 0.02 0.6 0.6	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32 0.58	8.9 18.4 464 0 8.4 0 1.6 0.01 0.51 0 0.52
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I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01 0.2 0.7 0.58 0.2 1.96	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27 0.04 0.3 0.55	III 8.21 15.3 58000 38.1 8.1 0 0 2 0.14 0.2 5.37	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5 0.25 0.2 0.52	$\begin{array}{c} 7.65\\ 22.8\\ 974\\ 0.3\\ 7.5\\ 0\\ 17.72\\ 0.17\\ 0.06\\ 0.5\\ 0.93\\ 0.1\\ 0.1 \end{array}$	MI II 7 24 1016 0.3 5.9 0.13 2 0 0.11 0.1 5.15	III 7.4 19. 135 0.5 4.4 0.0 3.5 0 0.4 0.1 0.5	7 72 3 2 7	7.9 21.1 1293 0.4 5.2 0 2.6 0 0.52 0 0.49	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07 0.27 0.6 0.53 0.5 0.33	II 8.08 26.7 405 0 6.4 0 5.2 0.02 0.02 0.02 0.6 0.6	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32 0.58	8.9 18.4 464 0 8.4 0 1.6 0.01 0.51 0 0.52
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I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01 0.2 0.7 0.58 0.2 1.96 10934 485 373	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27 0.04 0.3 0.55 26.8	III 8.21 15.3 58000 38.1 8.1 0 0 2 0.14 0.2 5.37 2.9	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5 0.25 0.2 0.52 1.2	$\begin{array}{c} 7.65\\ 22.8\\ 974\\ 0.3\\ 7.5\\ 0\\ 17.72\\ 0.17\\ 0.06\\ 0.5\\ 0.93\\ 0.1\\ 0.1\\ 70\\ 3.89\\ 70.8 \end{array}$	MI II 7 24 1016 0.3 5.9 0.13 2 0 0.11 0.1 5.15 0.4	III 7.4 19. 13. 0.5 4.4 0.0 3.5 0 0.4 0.1 0.5 0.3	7 72 3 2 7	7.9 21.1 1293 0.4 5.2 0 2.6 0 0.52 0 0.52 0 0.49 0.1	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07 0.27 0.6 0.53 0.5 0.33 243 11.5 37.3	II 8.08 26.7 405 0 6.4 0 5.2 0.02 0.02 0.02 0.6 0.6 0.3	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32 0.58	8.9 18.4 464 0 8.4 0 1.6 0.01 0.51 0 0.52 0.2
I 7.91 29.2 53500 35.5 4.7 0 6.64 4.01 0.2 0.7 0.58 0.2 1.96 10934 485	II 7.9 27 52100 34.3 4.5 0.033 2.5 2.27 0.04 0.3 0.55 26.8	III 8.21 15.3 58000 38.1 8.1 0 0 2 0.14 0.2 5.37 2.9	IV 8.12 20 54000 35.3 8.9 0.03 0 4.5 0.25 0.2 0.52 1.2	7.65 22.8 974 0.3 7.5 0 17.72 0.17 0.06 0.5 0.93 0.1 0.1 70 3.89	MI II 7 24 1016 0.3 5.9 0.13 2 0 0.11 0.1 5.15 0.4	III 7.4 19. 13. 0.5 4.4 0.0 3.5 0 0.4 0.1 0.5 0.3	7 72 3 2 7	7.9 21.1 1293 0.4 5.2 0 2.6 0 0.52 0 0.52 0 0.49 0.1	7.94 30.1 1800 0.7 6.4 0.23 3.1 0.07 0.27 0.6 0.53 0.5 0.33 243 11.5 37.3 39.7	II 8.08 26.7 405 0 6.4 0 5.2 0.02 0.02 0.02 0.6 0.6 0.3	III 8.45 13.9 690 0.1 6.6 0 41.2 0.32 0.58	8.9 18.4 464 0 8.4 0 1.6 0.01 0.51 0 0.52 0.2
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Measurements of EC and pH were made in the field using a pH/Cond 340i WTW meter. For the pH measurements the electrode was calibrated against pH buffers at each location. Aliquots were filtered through a 0.45-mm Millipore cellulose type membrane and stored in HDPE bottles. The sample bottles were rinsed three times with the filtered sample water before they were filled. Then, 0.25 ml/L of HNO3 (nitric acid) was added to the first aliquot to prevent precipitation. The samples were refrigerated at 4° C until analysis. The samples were



analyzed in the laboratory of General Directorate of Mineral Research and Exploration (MTA) of Turkey in Ankara. Cations were analyzed by inductively coupled plasma (ICP) and anions by ion chromatography (IC). SiO_2 was analyzed mainly by visible spectrophotometer. Bicarbonates were determined by titration in the laboratory. Heavy metals and other pollutants in water were measured with Hanna C200 multiparameter photometer. Hanna C 200 Series is a line of 15 different bench, microprocessor based photometers that measure up to 46 parameters in water and wastewater. Followed by water quality analysis, thematic maps were generated and digitized using MapInfo GIS software, where spatial analysis and integration were carried out for drinking and irrigation water quality mapping in the basin.

The measured pollutant are compared with the Turkish Water Pollution Control Regulation (2001) and with the international standards like WHO (1996) and EPA (1995).

4. DISCUSSION

A lack of sewage disposal and of solid waste disposal systems is threatening water resources in urban areas. In all towns on the Göksu delta, there is no domestic waste collection. Thus, waste disposal create serious pollution of groundwater and surface water resources, especially where there is no control of waste disposal in or near bodies of water. Unfortunately, most sewage with pollutant levels above the level permitted by national standards is allowed to drain into natural bodies of water without any treatment, thereby polluting most creeks and Göksu river in and near Silifke city, because there was not any sewage treatment plants until 2007. In 2007 a new sewage treatment plants was established in Silifke city.

The land in Göksu Delta is used widely agriculturally (Fig. 2). Agricultural practices result in non-point-source pollution of surface water. Such sources include fertilizer and manure applications to increase grain yield and income, farmers are currently decreasing their use of organic fertilizer in favor of inorganic fertilizers with improper proportions of nitrogen, phosphorous, and potassium. The drainage water and irrigation return flow transport the fertilizer into groundwater and surface water. In the study area, the consumption of fertilizers amounts to 520 kg/ha.

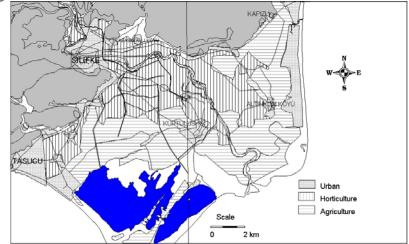


Figure 2. Land use on the Göksu Delta

Concentrations of major chemical elements in the surface water were related to the distance downstream from the source of the river, with surface water in the upstream reaches of good quality, but the river from Silifke city to the Mediterranean Sea is seriously polluted.

There was a wastewater outlets until 2007 that discharge a total of 10700 m^3 /day into the river from Silifke city, which, combined with the agricultural activities, were found to be the major causes of water pollution. In addition, there are much wastewater outlets from the town that discharge into the Göksu River between Silifke city and Mediterranean Sea. On all the 365 days of the year, fecal matter, waste clothes, food materials can be observed at sampling station Sökün Bridge (Fig. 1). However, the surface water samples are characterized by a high degree of variability with respect to EC, which ranges from 335 to 58000 μ S/cm. All the major ions and indicator for pollution such as salinity, NO₃, NH₃, PO₄ and some of the heavy metals also increased sharply



downstream from Silifke city to Mediterranean Sea. The water of Akgöl Lake is unaffected from the anthropogenic activities in the study area and has Mg-Ca-HCO₃ character. But Paradeniz Lake is a saltwater lagoon connected to the sea and the chemistry of Paradeniz water is similar to the Mediterranean Seawater. The water type of Göksu River is Ca-Mg-HCO₃ in upstream but after the Silifke it changes and the Na and Cl ions are added in the types of groundwater (Table 2, Fig 3 and 5).

Table 2. Chemical characters of su	rface waters	
Sample	Location	Chemical character
ME-17	Göksu, before reaching to Silifke	Ca-Mg-HCO3
ME-19	Akgöl Lake	Mg-Ca-HCO3
ME-22	Paradeniz Lake	Na-Cl
ME-6	Mediterranean Sea	Na-Cl
ME-7	Olukbaşı spring	Ca-Na-Mg-HCO3-Cl
ME-8	Göksu after Silifke	Na-Mg-Cl-HCO3

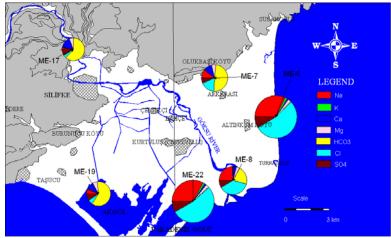


Figure 3. Thematic map for chemical characters of surface waters

The consantrationaly the chemical oxygen demand and dissolved oxygen are 22 and 7.1 mg/L at the sampling point ME-17 (upstream) and they changed to 137 and 6.4 at the sampling point ME-8 (downstream) (Fig. 4). The comparison of the chemical analyses of sampling points ME-17 and ME-8 indicate that the pollution is from Silifke city. This is deduced especially from the values of electrical conductivity and salinity. Except these the concentrations of NO₃, NH₃ and PO₄ increase due to agricultural activities and sewage.

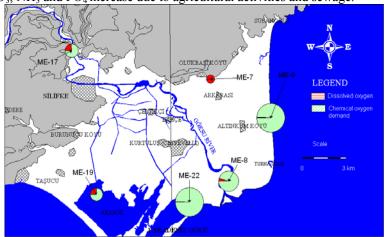


Figure 4. Thematic map for dissolved oxygen and chemical oxygen demand of surface waters

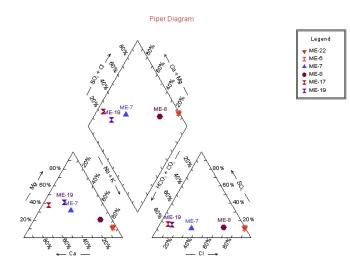


Figure 5. The Piper diagram

Agricultural activities are the main source for nitrate pollution in water (Carey and Llyod, 1985, De Simone and Howes, 1998, Gusman ve Marino, 1999; Birkinshaw ve Ewen, 2000; McLay et al, 2001; Ledoux et al., 2007; Oyarzun et al., 2007). Nitrate is very mobile in water (Meisinger and Randall, 1991; Birkinshaw and Ewen, 2000; Shamrukh et al, 2001). A high concentration of nitrate is generally attributed to anthropogenic sources. As Göksu Delta is surrounded by an area rich in citrus orchards, traditional farms and greenhouses, an agricultural source for NO_3 and SO_4 is possible. Use of fertilizers and pesticides is very widespread practice for agricultural activities in the area. The occurrence of high concentrations of nitrate and sulfate in all periods samples also coincides with the highest irrigation frequency (during the early periods of plant/vegetable development). The range of nitrate is found to vary between 0 to 41.2 mg/l. NO₃ concentration in this region is higher than Turkish limit value of 22 mg/l. The chemical analyses for nitrate for April 2008 show that the highest concentration is found in sampling point ME-8 (Sökün Bridge) where the land was intensively agricultural used (Fig 1 and 2). The phosphate concentration gives the similar results (Table 1). As indicated by Alloway (1995) the heavy metal sources of intensive farming regions could be mineral fertilizers (Cd, Cr, Mo, Pb, U, V, Zn) and pesticides (Cu, As, Pb, Mn, Zn). Cetinkaya (1996) reported that about 94 ton pesticides and 431 ton mineral fertilizers were used within a year at Goksu Delta . The pesticides and fertilizers contain also some heavy metals such as F, Br, Sn, Cl, Cu, Mn, Fe, Z Se, Co, Cd, Mo, Ni Pb and these are the source of water pollution. The Cr concentration of the river water is increased from 0 to 0.021 mg/l at the sampling point ME-8. Iron and cupper concentrations are also increased from 0 to 0.69 and 0.31 mg/L in down stream, respectively. These high heavy metal concentrations found at sampling point ME-8, may be related to the agricultural activities.

A model regarding DO (dissolved oxygen) and BOD (biochemical oxygen demand) was developed to assess the extent of pollution load in river Göksu. For the study of water quality modeling of river Göksu, water samples were collected from different sampling stations in February 2007 (Fig 6 and Table 3).

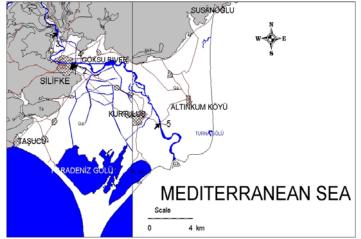
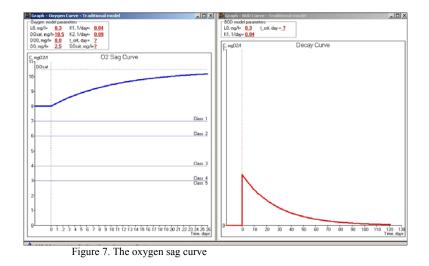


Figure 6. Map showing the water sampling locations for BOD-DO modeling

Table 3.	Results of analys (1) West sewer system	ses for BOD-DO (2) Mixing point	modeling (3) Regulator (before Silifke city) Upstream	(4) West sewer system	(5) Sökün bridge (after Silifke city) Downstream
pН	7,69	8,16	8,53	7,4	8,35
Temperature ^o C	17	13	13.6	17.9	13.6
Electrical conductivity µS/cm	1591	405	393	1330	382
salinity	0.6	0	0	0.5	0
Dissolved oxygen (DO) (mg/L)	0.1	7.9	8	0	7.2
Biological oxygen demand (BOD) (mg/L)	318	4	0	315	0

BOD-DO River models deal with the oxygen household conditions of the river, by considering some of the main processes that affect dissolved oxygen (DO) concentrations of the water. These models are of basic importance since aquatic life, and thus the existence of the aquatic ecosystem, depend on the presence of dissolved oxygen in the water (Jolánkai G., 2000). The main process that affect (deplete) the oxygen content of water is the oxygen consumption of microorganisms living in the water, while the decompose biodegradable organic matter. Among external sources anthropogenic ones are of major concern and this include waste water (sewage) discharges and runoff induced non-point sources of diffuse loads of organic matter. Another main process in the oxygen household of streams is the process of reaeration, the uptake of oxygen across the water surface due to the turbulent motion of water and to molecular diffusion. These two counteracting processes are considered in the traditional BOD-DO model (Streeter and Phelps, 1925) on the mathematical form. The wastewater discharge into the Göksu River from Silifke city is a total of 10 700 m³/day. The dilution equations compute the initial concentration of BOD as 0.29 and DO as 7.99 mg/L in the river downstream of point source sewage discharge, with the assumption of instantaneous mixing. This calculated dissolved oxygen contends is similar with the measured contend at mixing point and this is important for the calibration of the model. The initial oxygen deficit (for 13.6° C) of the water is calculated as 2.5 mg/L. The oxygen sag curve has a critical point where the DO content of water is the lowest that is when the oxygen deficit is highest. The result of modeling show that, there is not occurred a critical point in Göksu River, the reason is the hipher flow rate of Göksu river (Fig. 7).



5. CONCLUSIONS

The ion and pollutant concentrations in the water of Göksu River change before and after Silifke city, making the water in the study area unsuitable for use in irrigation. The substances released by humans include industrial wastes, domestic sewage, rubbish, organic and inorganic fertilizers, and pesticides, which include a range of substances that are harmful to humans. These pollutants transported to surface water in various ways, leading to deterioration of water quality.

Waters in the river at the mountain and piedmont sites are of good quality with the EC below 500 μ S/cm. However, the organic pollutants, including COD, BOD NH₃ and NO₃ followed sharply increasing trends from Silifke city to Mediterranean Sea. The chemical character of Göksu river water changes after the Silifke city and also the COD increases from 22 mg/L to 137 mg/L, DO decreases from 7.1 to 6.4 mg/L in downstream. These are the indicators for urban pollution from Silifke city. The range of nitrite is found to vary between 0 to 1.31 mg/L. NO₂ concentration in the surface waters of Göksu delta is higher than Turkish limit value in some periods. The range of nitrate concentration is found to vary between 0 and 41.2 mg/L for 2006-2008 and the ammonium in the water of Paradeniz Lake is determined between 0 and 15.68 mg/L. Comparing these concentrations with Turkish standard shows that in many points exceed the limits. The range of phosphate is found to vary between 0 to 0.88 mg/L. Phosphate concentration in this region is also higher than Turkish standard.

The F concentration of the surface water is changed between 0 and 2 mg/L during 2006 and 2008 sampling. Comparing this concentration with Turkish standard (1 mg/L) show that in many sampling points exceed the limit is exceeded. The range of iron is found to vary between 0 to 0.94 mg/L. Fe concentration in this region is higher than EPA limit value of 0.3 mg/L. Fresh water contains in general no copper. The copper concentrations of the samples change between 0.0 and 2.81 mg/L, and it exceeds the limit value of 0.05 mg/L of Turkish standard. The Cr and Mn concentrations of the surface water change between 0 and 0.05 mg/L and between 0 and 3.4 mg/L, respectively.

Agricultural sources of pollution focused on pesticide and fertilizer use. The source of excess concentration of various heavy metals is the agricultural activities and fertilizers. In the present study, the GIS technique has successfully demonstrated its capability in surface water quality mapping of the Göksu Delta. The final output has given the pictorial representation of water quality suitable or unsuitable for irrigation purposes in the basin. From the photometric heavy metal analysis, it is inferred that the excess concentration of some pollutants at some locations is the cause of undesirable quality for irrigation purposes. The source of excess concentration of various heavy metals is the agricultural activities and fertilizers. More rational use of fertilizers and pesticides will reduce their impacts on the water resources. It is determined that the heavy metals and other pollutants in the fertilizers and pesticides are transported easily to river water with irrigation return flow in the vicinity of Kapızlı, Altınkum and Kurtuluş towns. There was not a waste water treatment plant until 2007 in Silifke city; in addition, in all towns in Göksu Delta, there is not any domestic waste collection. Thus, waste disposal create serious pollution for Göksu River water. The water quality of Göksu River is modelled and determined that the



waste water discharge of 10700 m3/day from Silifke city does not create a serious problem because of the high amount of flowrate of Göksu river. No critical point occurs where the DO content of water is lowest.

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MODELING THE DRILLING PROCESS OF SOME AL-MG-CU ALLOYS AND AL-MG-CU/SIC COMPOSITES USING ARTIFICIAL NEURAL NETWORK

Mohammed T. Hayajneh Industrial Engineering Department, Faculty of Engineering Jordan University of Science and Technology Irbid, Jordan hayajneh@just.edu.jo

Adel Mahamood Hassan Industrial Engineering Department, Faculty of Engineering Jordan University of Science and Technology Irbid, Jordan adel@just.edu.jo

Ahmad Turki Mayyas Industrial Engineering Department, Faculty of Engineering Jordan University of Science and Technology Irbid, Jordan mayyas111@just.edu.jo

Abdalla Alrashdan Industrial Engineering Department, Faculty of Engineering Jordan University of Science and Technology Irbid, Jordan alrash@yahoo.com

Abstract: Machining of metal matrix composites (MMC's) is very important process and has been a major problem that attracts many researchers to study of characteristics of MMC's during machining process like turning, milling and drilling. This paper concerns with the potential of using feed forward backpropagation neural network in prediction of torque and thrust force during dry drilling of aluminum-copper/silicon carbide composites produced by stir casting method. The effect of the addition of copper as alloying element and silicon carbide as reinforcement particles to Al-4wt.% Mg metal matrix has been investigated by using artificial neural networks. The mean absolute relative errors between experimental and predicted values from network were 2.03% for torque, and 3.46% for thrust force. Therefore, it is suggested that by using ANN outputs, it is possible to predict the results of cutting parameters in drilling process which will be in a good agreement with the experimental ones.

Keywords: Aluminum, Artificial Neural Network (ANN), Casting, Drilling, Metal matrix Composites (MMCs)

1 Introduction

Metal-matrix composites (MMCs) are new class of materials that consist of a non-metallic phase distributed in a metallic matrix with properties that are superior to each of the constituent used (Tosun&Muratoglu,2004).Composite materials are usually classified on the basis of the physical or chemical nature of the matrix phase, e.g., polymer matrix, metal-matrix and ceramic matrix composites.

Particulate metal matrix composites (PMMC) are cheaper in both raw materials and fabrication processes and have potential for applications requiring relatively large volume production. The relative ease of fabrication of MMCs is also another favorable factor. As they can be produced by many well known methods, such as casting, powder metallurgy, and metal spray processes (Tosun&Muratoglu,2004). All such processes are readily available for manufacturing unreinforced alloys. In addition, the use of a secondary process, such as rolling, forging, extrusion and heat treatment, can be applied only to improve properties of composites without incurring significant damage to the reinforcement (Tosun&Muratoglu,2004).

Aluminum matrix composites (AMCs) refer to a class of light weight and high performance aluminum centric material systems. The reinforcement in AMCs could be in the form of continuous/discontinuous fibers, whisker or particulates, in volume fractions ranging from a few percent to 60% [3], they are usually reinforced

by Al₂O₃, SiC, and C (Tosun&Muratoglu,2004; Candan&Bilgic,2004; Wain,Thomas,Hickman,Wallbank&Teer,2005; Ramulu, Rao&Kao,2002). Properties of AMCs can be tailored to the demands of different industrial applications by suitable combinations of matrix, reinforcement and processing route. In the last few years, AMCs have been utilized in high-tech structural and functional applications including aerospace, defense, automotive, sport instruments and thermal management areas.

However, because of the poor machining properties of MMCs, drilling of such materials is considered as a challenging task for manufacturing engineers. Unlike machining of conventional materials, many problems are presented during drilling of MMCs, such as tool wear and burr(Ramulu,Rao&Kao,2002;Cotterell&Kelly,2002; Monaghan&Reily,1992;Kilickap,Akır,Aksoy&Inan,2005). Cutting forces during drilling of aluminum are generally low and because aluminum is a good conductor of heat and since most aluminum alloys melt at relatively low temperatures (i.e. less than 660 °C), cutting temperatures and tool wear rates are also low (Ramulu,Rao&Kao,2002;Cotterell&Kelly,2002). When cut under proper conditions with sharp tools, aluminum alloys acquire fine finishes through turning, drilling and milling, minimizing the necessity for grinding and polishing operations. Aluminum is commonly machined with high speed steel, diamond and carbide tooling; silicon nitride based ceramic tools are generally not used with aluminum because of the high solubility of silicon in aluminum (Cotterell&Kelly,2002). The major machinability concerned with aluminum alloys includes tool life, chip characteristics, chip disposal and surface finish (Cotterell&Kelly,2002).

The final surface finish expressed as surface roughness, Ra, during the machining of Al/SiC MMC's is much lower than that obtained during the machining of the matrix alloy alone(Tosun&Muratoglu,2004; Monaghan&Reily,1992;Kilickap,Akır,Aksoy&Inan,2005). Monaghan & Reily(1992) attributed the improved surface finish to the burnishing or honing effect produced by the action of small SiC particles trapped between the flank face of tool and the workpiece surface.

The use of artificial neural networks (ANNs) represents a new methodology in many different applications of composite materials including prediction of mechanical properties of aluminum based materials (Durmus,Ozkaya&Meric,2006;Altinkok&Koker,2005;Altinkok&Koker,2006;Zhang,Friedrich&Velten,2002;Ga nsen,Raghukandan,Kathikeyan&Pai,2005;Lee,Almond&Harris,1999)It is a promising field of research in predicting experimental trends and has become increasingly popular in the last few years as they can often solve problems much faster compared to other approaches with the additional ability to learn from small experimental data. Forouzan and Akbarzadeh (2006) used ANN in prediction the effect of thermo-mechanical parameters on mechanical properties of aluminum alloy AA3004. They found that well-trained ANN models provide fast, accurate and consistent results, making them superior to all other techniques. Lin, Bharracharyya&Kecman (2003) used ANN and multiple regression methods in analyzing machining parameters of aluminum alloy reinforced with silicon carbide particles with attention on tool wear. They found that ANN has ability to predict tool wear accurately from feed force.Genel, Kurnaz&Durman (2003) used multiple-layer feed-forward artificial neural network (ANN) modeling for tribological behavior of short alumina fiber reinforced zinc-aluminum composites. The specific wear rate and coefficient of friction obtained from a series of the wear tests were used in the formation of training sets of ANN (Genel,Kurnaz&Durman,2003). They found that ANN is an excellent prediction technique for both parameters if it is well trained.

2 EXPERIMENTAL SETUP AND PROCEDURE

2.1 Materials

The test materials studied in this work were a mixture of aluminum (commercial grade Al, ~99% purity) and copper granules with an average particle size of 0.425 mm and ~97% purity as a matrix and silicon carbide as reinforcement particles. About 1000 g of commercial grade Al ingots and different weight percentages of copper powder (0, 1, 2, 3, 4, and 5 wt.%) was taken to prepare the base metal matrix by casting method. Specific quantities of silicon carbide powder with an average particle size of 75µm and purity exceeds 99.5% of 5 and 10 vol.% were added to the matrix alloy. Finally, magnesium (~99% purity ingots) added in small quantities (fixed weight percentage 4wt.%) in the final stage to promote wettability between metal matrix and reinforcement particles (Candan&Bilgic,2004; Hassan,Tashtoush&Alkhalil,2007)

2.2 Processing

The synthesis of the particulate metal matrix composites used in the present study was carried out by the stir casting method (compocasting method). Aluminum ingots and copper granules melted together at 850 °C. The amount of SiC powder pre-oxidized at 900°C for about 30 minutes to form a layer of SiO₂ on their

surface in order to improve their wettability with molten aluminum(Maghanaki,Lajevardi&Akhlagi,2004; Tekman, Ozdemir, Cocen & Onel,2003). were incorporated into the melt. Mg added to the melt in the final stage prior to pouring task to enhance the wettability between metal matrix and reinforcement particles. The pouring temperature was maintained at 580-600 °C in semisolid state. Then the mould was left in air to cool down to room temperature. Finally the obtained cast bars turned to small specimens of 25 mm diameter and 40 mm in length to be used in the drilling experiments.

2.3 Drilling Test

There are many types of drills but the simplest and most often used is the twist drill. This drill is simple and cheap to produce but its cutting geometry is complicated (Wyatt&Trmal,2006). The drilling test was carried out on a vertical machining center (Q&S Drillmaster, England). A general purpose 8.5 mm diameter high speed steel (HSS) twist drills (U.fA Germany) were utilized in the drilling process. The test was carried out under predetermined machining parameters with cutting speed of 300 rpm and feed rate of 0.229 mm/rev without using any lubricants.

The drilling torque and thrust force were measured with a multi-component dynamometer (TeLC BKM2000, Germany). The dynamometer signals were then processed to make them suitable for computer capture. This was achieved via charge amplifiers and an analog to digital (A/D) converter, then to the computer. The surface finish of each drilled hole was measured using Taylor-Hobson (Surtronic 3P) type instrument. Surface roughness readings were taken at least at three positions spaced at 120° intervals around the hole circumference and approximately mid-way down the depth of the hole and the averaged values were used in the training of the ANN. Quanta 200 Digital scanning electron microscopy (SEM) was used to analyze the quality of drilled holes in some investigated specimens.

3 MODELING WITH NEURAL NETWORKS

Artificial neural networks (ANN) are considered as artificial intelligence modeling techniques. They have highly interconnected structure similar to brain cells of human neural networks and consist of large number of simple processing elements called neurons, which are arranged in different layers in the network. Each network consists of an input layer, an output layer and one or more hidden layers. One of the well-known advantages of ANN is that the ANN has the ability to learn from the sample set, which is called training set, in a supervised or unsupervised learning process. Once the architecture of network is defined, then through learning process, weights are calculated so as to present the desire output (Rogier&Geatz,2003; Negnevitsky,2005)

3.1 Data Set and Processing

The input to individual ANN nodes must be numerical value and fall in the closed interval [0, 1]. Because of this conversion method the normalization technique was used in the proposed ANN according to the following formula:

Normalized value=
$$\frac{\text{input value} - \text{minimum value}}{\text{maximum value} - \text{minimum value}}$$
(1)

Output values resulted from ANN also in the range [0, 1] and converted to their equivalent values based on reverse method of normalization technique.

3.2 Learning rules and validation

Neural networks are adaptive statistical devices. This means that they can change the values of their parameters (i.e., the weights) as a function of their performance. These changes are made according to learning rules which can be characterized as supervised (when a desired output is known and used to compute an error signal) or unsupervised (when no such error signal is used). Sigmoid function is the most common activation function in ANN because it combines nearly linear behavior, curvilinear behavior, and nearly constant behavior, depending on the value of the input [22-24]. The sigmoid function is sometimes called a squashing function, since it takes any real-valued input and returns an output bounded between [0, 1]; (Rogier&Geatz,2003; Negnevitsky,2005)

$$v = f(x) = \frac{1}{1 + e^{-x}}$$
(2)

Back propagation neural networks represent a supervised learning method, requiring a large set of complete records, including the target variables. As each observation from the training set is processed through the

network, an output value is produced from output nodes. These values are then compared to the actual values of the target variables for this training set observation and the errors (actual-output) are calculated. Normalized root mean square error value (NSE) was used to evaluate the training performance of the ANN (Abdelhay,2002):

$$NSE = \sqrt{\frac{\sum (\theta - \theta_0)^2}{\sum \theta^2}}$$
(3)

Where θ can be the experimental value of torque or thrust force and θ_{θ} represents the predicted output value for each output node. More details about back-propagation training algorithm are included in literature(Altinkok&Koker,2005;

Gansen, Raghukandan, Kathikeyan & Pai, 2005; Frouzan & Akbarzadeh 2006; Rogier & Geatz, 2003; Negnevitsky, 2005; Abdelhay, 2002).

4 RESULTS AND DISCUSSION

The purpose of the present work was to determine the effect of the addition of alloying element (copper), and reinforcement particles (silicon carbide), on aluminum drilling process. The most important factors, which determine the condition of the work material that can influence the outcome of the machinability, are Lin,Bharracharyya&Kecman,2003)alloy chemistry, additions, physical and mechanical properties, morphology, size and volume fraction of the constituent phases, microstructure (grain refining and modification), porosity, and heat treatment.

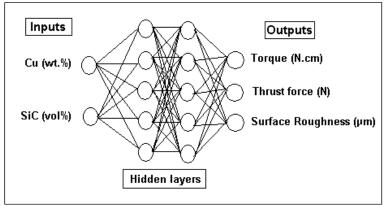
4.1 ANN structure and results

The ANN was implemented using fully developed feed forward back propagation network. For the training problem at hand the following parameters were found to give good performance and rapid convergence: two input nodes; namely: Cu (wt.%) and SiC (vol.%), two hidden layers with 5 neurons and three output neurons (torque, thrust force and surface roughness). Sigmoid activation function was selected to be the transfer function between all layers. The ANN architecture is shown in Fig. 1.

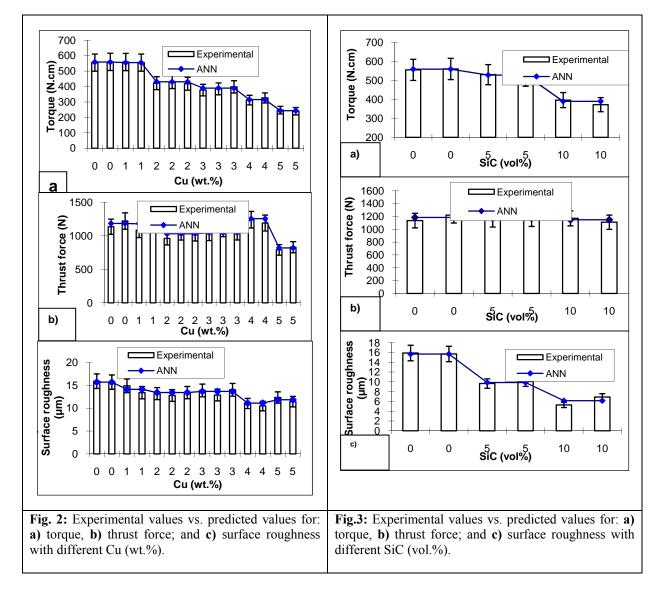
A total dataset consists of 42 samples was used to train and test the network. Among them 32 samples were used in training process and 10 used in testing process. This dataset was obtained from compocasting process and considered as cast samples without any further post treatment except cleaning and cutting of the obtained bars. After many trials, learning rate and momentum are experimentally selected to be 0.65 and 0.20, respectively.

However, the main quality indicator of a neural network is its generalization ability, its ability to predict accurately the output of unseen data and this was achieved by testing data set. Absolute relative errors between experimental and predicted values from ANN were used to evaluate the performance of the proposed ANN in prediction technique. The mean absolute relative errors were: 2.03% for torque, 3.46% for thrust force, and 6.48% for surface roughness. The maximum absolute relative errors were 8.42% for torque, 12.02% for thrust force and 29.55% for surface roughness. However, the highest value of error corresponds to surface roughness could be processed as outlier point which appeared due to large variation as a result of drilling process and/or surface finish testing due to nature of aluminum based surfaces which consider as ductile material. This level of error is satisfactory and smaller than errors that normally arise due to experimental variation and instrumentation accuracy.

Fig. 2 shows the comparison between experimental torque, thrust force and surface roughness values and corresponding ANN outputs for Al-4wt.%Mg-Cu alloys. While Fig. 3 shows the comparison between experimental torque, thrust force and surface roughness values and corresponding ANN outputs for Al-4 wt.%Mg-SiC composites. The columns represent measured values with $\pm 10\%$ error interval and continuous line represents ANN output. The ANN outputs seem to be in a good agreement with experimental values.







4.2 Effect of copper and silicon carbide addition on the drilling of aluminum

Hardness is one of the most important metallurgical parameters that can control the material machinability. In fact, aluminum alloys differ from many other metals in that the machinability of aluminum

generally improves as the hardness increases. Most automotive machine shops agree that a minimum hardness of 80 Brinell is desirable (Tash, Samuel, Mucciardi&Doty, 2006). Copper and magnesium increase alloy hardness, improve the machined surface finish, and decrease the tendency of the alloy to build up on a cutting tool edge. Magnesium hardens the alloy matrix and, by doing so, reduces the friction coefficient between tool and workpiece which, in turn, results in shorter and tighter chips, and thus provides a better surface finish (Negnevitsky, 2003, Zhang, Friedrich & Velten, 2002). In the drilling results, it was also found that a lower copper content resulted in higher cutting forces (both torque and thrust force) (Zhang, Friedrich & Velten 2002). Fig. 2 shows the effect of Cu (wt.%) on the resulted torque, thrust force, and surface roughness of Al-based alloys, respectively. It is obvious that both torque and thrust force were lowered when the amount of copper was increased in the Al-4wt.%Mg matrix alloy. Also, a small addition of Mg improves the alloy machinability, lowering the cutting force and torque Lin, Bharracharyya&Kecman, 2003; Tash, Mucciardi, Samuel, Valtierra&Doty, 2006)

Fig. 3 shows the experimental versus predicted values of different Al/SiC composites. The general trend of machinability which can be drawn from these figures can be stated as: when the amount of SiC increases in the metal matrix, the resulted machinability is improved (mainly by lowering torque) of Al-4wt.%Mg alloy. This may be attributed to the smearing of the softer Al- 4 wt.%Mg metal matrix to the cutting tool compared to the harder matrix containing SiC particles. This is valid for lower volume fractions of reinforcement particles; however, higher volume percentages of silicon carbide will also result in higher cutting forces compared to the matrix alone due to the presence of harder ceramic particles. Improvement in the surface finish was observed due to the presence of SiC particles as shown in Fig. 6c. Tosun and Muratoglu(2004) studied the drilling process of Al/17 vol.%SiC using different cutting tools and drilling parameters. They found that as the speed and/or feed rate increased the thickness of the matrix layer increased. As the feed rate increased, the cutting temperature increased and this may cause weakening of the binding between the matrix and the SiC_P, thus the matrix softens, and motion of SiC occurred easily, and also the chips tend to be segmented easily with ductile tearing Tosun &Muratoglu,2004). The combined effect of increasing copper and silicon carbide amounts tends to improve the drilling of Al-Cu/SiC composites (lower values of torque and thrust force) compared to Al- 4 wt.%Mg alloy.

5 CONCLUSIONS

The aim of the present work was to illustrate the application of artificial neural network as prediction technique to estimate torque and thrust force as well as surface roughness of some Al-Mg-Cu alloys and their corresponding composites reinforced with 5 and 10 vol% of SiC in the drilling process. The ANN gives satisfactory results when compared to the experimental measurements. The mean absolute relative errors between experimental and predicted values from network were 2.03% for torque and 3.46% for thrust force,. Therefore, by using ANN values, satisfactory results may be estimated rather than measured and hence reducing testing time and cost.

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TENSILE PROPERTIES OF POLYPROPYLENE/METAL OXIDE NANO COMPOSITES

Mirigul Altan, Yildiz Technical University meksi@yildiz.edu.tr

Huseyin Yildirim Yildiz Technical University, husyil@yildiz.edu.tr

Alper Uysal Yildiz Technical University auysal@yildiz.edu.tr

Abstract

Polymers reinforced with nano metal oxides open up new pathways for engineering flexible composites that exhibit better mechanical and chemical properties. In this study, tensile properties of the polypropylene (PP) composites filled with nano titan dioxide (TiO₂) and zinc oxide (ZnO) were investigated. Nano particles were coated with maleic anhydride grafted styrene ethylene butylene styrene (SEBS-g-MA) and silane, respectively prior melt mixing for better surface adhesion and fine dispersion. Nano composites were obtained by using twin screw extruder at TiO₂ and ZnO loading of 1%, 3% and 5%. Firstly, thermal analysis was done to obtain melt temperature, crystallization temperature and degree of crystallinity. Then, tensile test was applied to obtain yield strength, tensile strength, elastic modulus and elongation of the composites. Due to the stiff structure of the metal oxides, all tensile properties except elongation were increased. On the other hand, although TiO₂ has higher hardness than ZnO, the elongation of the composites with TiO₂ was higher than that of with ZnO. This is probably due to the better compatibility of TiO₂ with SEBS-g-MA and this case induced more fine structure of TiO₂ with PP while ZnO particles agglomerated in some regions of the matrix which confirms the results of lower elongation and degree of crystallization.

Keywords: polypropylene, nanocomposite, titan dioxide, zinc oxide, tensile properties

1. INTRODUCTION

Polymers reinforced with nano metal oxides become popular every day because of their improved mechanical strength, flexibility in designing besides better chemical, electrical and optical properties (Breiner&Mark,1998; Omar,Ishak,Ismail& Fuad,1995; McCarthy & Mark,1998; Rong, Zhang, Zheng, Zeng & Friedrich,2001)

On the other hand, nano particles may agglomerate and thus degrade the properties of the nano composites. To overcome this problem, dispersant and coupling agents are being used (Tongpool, Kruenate

&Panyathanmaporn,2004). Furthermore, the decreasing of the impact strength due to the stiffness of the inorganic material is another problem generally encountered. Researchers use elastomeric nature materials to increase the toughness of the composites (Bao&Tjong,2007;Ishak,

Chow&Rochmadi,2008).In this work, tensile properties of the polypropylene reinforced with nano zinc oxide and nano titan dioxide were investigated. Improved tensile properties were obtained by using silane and SEBS-g-MA for better dispersion and surface adhesion between the metal oxide and the matrix.

2. EXPERIMENTAL WORK

2.1 Materials and Preparation of the Nano Metal Oxides

Polymer material used in this study was polypropylene copolymer (56M10, Sabic Company) with melt flow index of 6.2 g/10 min, density of 0.902 kg/cm³. Nano material was ZnO and TiO₂ (Nabond Company, China).



SEBS-g-MA (FG1901X, Kraton, Shell Company) and vinyltrimethoxysilane (VTMS, Aldrich) were used for coating the nano TiO₂ particles for better surface adhesion and dispersion.

The nano metal oxide particles were coated with them SEBS-g-MA and then silane, respectively. SEBS-g-MA was used as compatibilizer and by coating the powders with it, the coupling agent property of the SEBS-g-MA was thought to be more effective. Silane coating was for better dispersion of the SEBS-g-MA coated particles in the polymer matrix. Coating was applied by melt mixing of the nano particles with SEBS-g-MA which was dissolved in toluene in 48 hours at 25 °C. SEBS-g-MA coated nano powders were pulverized after drying the mixture at 50°C for 8 hours. Silane coating was applied by preparing a solution of 96% absolute alcohol and 4% distilled water with 1% silane. SEBS-g-MA coated nano particles was added slowly to this solution and mixed for 3 hours. The mixture was pulverized after drying at 50 °C for 8 hours.

2.2 Blending

The addition of the nano composites was applied in three different ratios as 1%, 3% and 5%. The coding of the composites was done as follows: $PP/1TiO_2$, $PP/3TiO_2$, $PP/5TiO_2$ and PP/1ZnO, PP/3ZnO, PP/5ZnO. The nano powders and the polymer were loaded into a twin screw extruder (Rondol MicroLab, England) with L/D ratio of 20. The operation temperature was set as 220, 200, 180, 120 and 75 °C and the speed of the screw was 60 rpm. The extrudate strands were granulized and dried at 80 °C under vacuum for two hours.

2.3 Differential Scanning Calorimetry (DSC)

The melting and crystallization behaviors were studied by differential scanning calorimetry (DSC, Perkin Elmer DSC-7) in nitrogen atmosphere. The samples (4-5 mg) were heated from 40 °C to 180 °C at 10 °C/min and held at 180 °C for 5 min and then cooled back to 40 °C at 10 °C/min and held 5 min at 40°C. Then, second heating cycle was performed to delete the thermal history of the samples. The melting temperature (Tm), crystallization temperature (Tc) and degree of the crystallization (Xc) were obtained. The fusion enthalpy of 100% crystalline phase of the PP was taken as 209 J/g in calculating the degree of the crystallization of the blends (Scheirs,2000).

2.4 Injection Molding

The dried granules of the composites were injection molded with a 40 tone injection molding machine. Tensile test specimens were obtained. The mold temperature was 40 °C, injection pressure was 65 MPa, holding pressure 45 MPa, holding time 15 s and cooling time was taken as 10 s.

2.5 Scanning Electron Microscope

Morphology of the fracture surface of the each specimen was analyzed by scanning electron microscope (JEOL JSM-5910 LV). The fracture surfaces obtained from the impact tests were etched with tetrahydrofuran (THF) and then washed with acetone and dried under vacuum. Finally, all the specimens were coated with gold.

2.6 Tensile Test

Tensile test was carried out by universal tensile machine (Zwick Z010) at room temperature according to ISO R-527. The speed of the cross head was 50 mm/min.

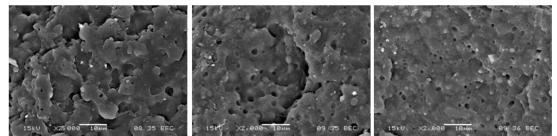
3. RESULTS AND DISCUSSION

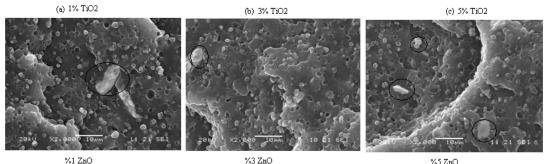
3.1 Thermal and Morphological Characterization

The DSC results of the composites are given in Table 1. Melt temperature (T_m) and crystallization temperature (T_c) did not change very much with the addition of TiO₂ and ZnO. On the other hand, ZnO addition reduced degree of crystallization more than that of TiO₂ which indicates that TiO₂ particles did not influence the stability of the PP. The retarding effect of zinc oxide on the PP crystals and the physical hindrance effect on the

molecular chains were more obvious in PP/ZnO composites. This effect is probably due to the better physical compatibility of TiO₂ with SEBS-g-MA and fine dispersion of the nano particles. There are many studies about the effects of nano particles on the degree of crystallization. Some of them accepted these particles as nucleating agents and some experimental observations showed diversified results (Chan, Wu, Li & Cheung, 2002; Li,Wei&Sue,2002; Ma, Zhang,Qi,Li&Hu,2002). For example, for nano CaCO₃ filled PP, the increasing nanofiller content did not affect the cyrstallinity (Chan, Wu, Li & Cheung, 2002). However, in other studies about clay/PP composites, crystallinity either increased (Li, Wei&Sue, 2002) or decreased (Ma, Zhang,Qi,Li&Hu,2002). Also, Chandramaouleeswaran et al (Chandramoulesswaran,Mhaske&Kathe,2007) found reduction in crystallinity of PP/nano ZnO composites similar to the obtained results in this study. Researches (Bahloul, Legare, David& Cassagnau, 2010; Zebarjad, Sajjadi, Tahani&Lazzeri2006) on nano titan dioxide reinforced composites generally reported that TiO₂ did not affect degree of crystallinity very much or behaved as nucleating agent (Garcia, Vliet, Jain, Schrauwen, Sarkissov&Boukamp, 2004; Wang, Wang& Zhang, 2009). The possible agglomers given in Fig. 1 within black circles strengthen the result of lower crystallinity of the ZnO composites. On the other hand, composites with reinforced TiO₂ gave more homogenous and fine dispersed morphological structures.

	Table 1. Thermal properties of the composites								
Blend	T_m (°C)	T_{c} (°C)	Enthalpy (J/g)	$X_{c}(\%)$					
Original PP	166,3	124,9	85,4	40,86					
PP/1TiO ₂	165,8	122,9	82,7	39,57					
PP/3TiO ₂	166,1	124,5	81,2	38,85					
PP/5TiO ₂	166,5	125,1	83,1	39,76					
PP/1ZnO	166,6	123,1	65	31,10					
PP/3ZnO	165,9	123,4	63,42	30,34					
PP/5ZnO	165,9	123,1	64,6	30,91					





%1 ZnO

Fig. 1. SEM images of PP/TiO₂ and PP/ZnO nano composites

3.2 Tensile Properties

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Metal oxides enhanced the mechanical properties of the polymer composites (Kruenate, Tongpool &Panyathanmaporn,2004).

Generally tensile properties such as tensile strength, elastic modulus, stress at break increase while elongation decreases(Bao&Tjong,2007; Garcia, Vliet, Jain, Schrauwen, Sarkissov&Boukamp, 2004). Representative stressstrain curves obtained from the tensile test are shown in Fig. 2. Although ZnO has more ductile character than TiO₂, the elongation of the PP/TiO₂ composites found in this study was higher than that of PP/ZnO composites. OISAI

This is probably due to the elastomeric material of SEBS-g-MA. SEB-g-MA showed more compatible structure with TiO_2 as discussed before in thermal properties. It is known that the interface between the polymer matrix and SEBS is strong due to the compatibility of their phases because SEBS could diffuse into the polymer under the formation of miscelles (Setz, Stricker, Kressler, Duscher & Mulhaupt, 1996).

Maleic anhydride functional groups grafted to the ethylene butylenes (EB) mid block of SEBS. Then, it becomes easier for the molecular chains of SEBS-g-MA and the polymer to bond with metal oxide. As result, the homogenous, fine dispersed structures can be obtained. However, according to the thermal analysis and tensile test results, SEBS-g-MA coated of ZnO particles were not dispersed as fine as TiO_2 particles. Fig. 3 gave the comparison of the effects of the two metal oxides on the tensile properties of the composites. Due to the stiff structure of the TiO_2 and better surface adhesion between the nano particle and the polymer matrix, yield strength, tensile strength and elastic modulus was higher than that of composites with ZnO. At 1% addition of the both metal oxides, an apparent increase was observed in the tensile properties except elongation. The increment in this ratio of the metal oxides was also very close to each other. At 3% and 5% loading of TiO_2 gave better results in every case.

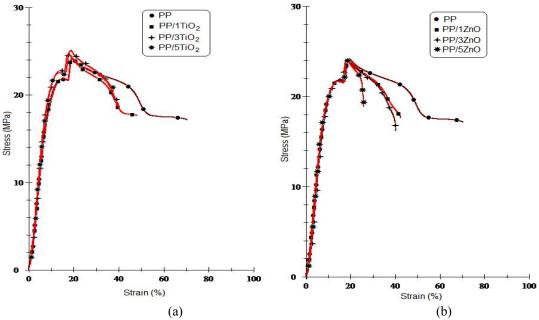


Fig 2. Stress-strain curves of the composites a) PP/TiO2 and b) PP/ZnO

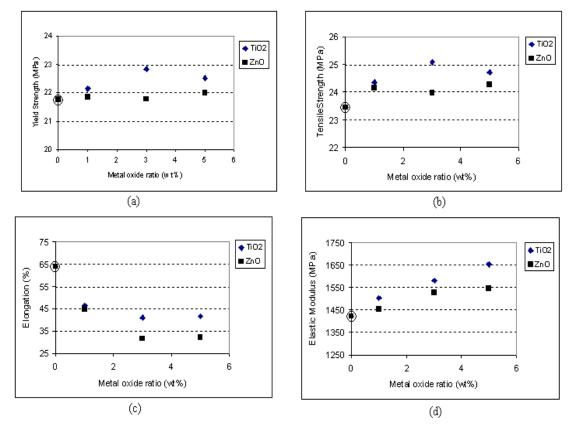


Fig. 3 Tensile properties of nano TiO₂ and ZnO reinforced PP (a-yield strength, b-tensile modulus, c- elongation d-elastic modulus), (I): original PP

4. CONCLUSION

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Metal oxides improve tensile properties but every metal oxide behaves different according to its physical, mechanical and chemical properties. In this study, two nano metal oxides were used as TiO₂ and ZnO for improving tensile properties of the polypropylene composites. SEBS-g-MA coating of the particles provided better surface adhesion besides fine dispersion together with silane. TiO₂ gave higher yield strength, tensile strength and elastic modulus due to its stiff structure and also its higher hardness than that of ZnO was effective in this result. On the other hand, elongation of the PP/TiO₂ composites was expected to be lower when compared with ZnO reinforced composites but just the opposite was obtained especially in the ratios over %1. This shows the compatibility of SEBS-g-MA was better with TiO₂ than ZnO. Furthermore, ZnO agglomerates appeared in some regions of the matrix reduced the tensile properties also crystallinity of the PP/ZnO composites.

5. ACKNOWLEDGMENT

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WHICH SEARCH ENGINE IS THE MOST USED ONE AMONG UNIVERSITY STUDENTS?

Nadire Cavus, Kezban Alpan Department of Computer Information Systems Near East University, Cyprus nadirecavus@neu.edu.tr, kezban alpan@yahoo.com

Abstract: The importance of information is increasing in the information age that we are living in with internet becoming the major information resource for people with rapidly increasing number of documents. This situation makes finding information on the internet without web search engines impossible. The aim of the study is revealing most widely used search engine among university students. The investigation described in the study was carried out with 300 random voluntary students. The results obtained were analyzed using descriptive methods and constructed. The results indicated that Google is the most widely used search engine by students. To enlarge the scope of the research, number of universities and students might increase. The results of this study add empirical data to the relevant field and are expected to help computer science students, experts, instructors, and everyone else who wants to reach information via the internet.

Keywords: Search engine; information retrieval; internet; Google; Yahoo; Bing, Ask, AOLSearch.

1. INTRODUCTION

Search engine is an information retrieval system based web site that helps users to retrieve any information from huge internet database and it is a kind of tool that crawls in the web according to user direction and it will record everywhere it has been and everything user look for (Capra & Quinones, 2005). The search engine software is a kind of information retrieval program and it has two major task: Searching through the billions of terms recorded in the index to find matches to a search and ranking retrieved records in order to decide most relevant (Chowdhury, 1999) Usually, internet users prefer search engines to access required information from the internet because search engines are open for public use with billions of web sites and during last years, there are many important researches about this area. Bases of search engines are information retrieval systems which are improving for 50 years but according to architecture and process specifications, search engines shows some differences form information retrieval systems (Lavrence & Giles, 1999).

One of the main components of search engine is a robot which is called as Web Crawler (or Spider) and it works as a network surfer and it downloads a searched web site to local disk. Web crawler is a kind of computer program that browses the Web in a methodical, automated way (Hu et al., 2001). This process is called as Web Crawling or spidering. Search engines use spidering to provide up-to-date information. The most important aim of web crawler is copying all visited web pages for later searches to make next searches faster. Web crawlers can also used for automating maintenance task on a web site like checking links or validating code. Also web crawlers are used to collect specific information from Web pages (Batzios et al., 2007). Even web crawlers are very easy programs, they finds million of documents and helps to IR systems to retrieve correct information in easy way. Also sometimes, crawler can find the information which is hiden by website owner or webmaster. Because of this, many web crawlers has to work according to robots exclusion protocol. Some search engines use more than one web crawler for different purposes but not all web crawlers are works to find information. Web crawlers also may work as link checker, page change monitor, validator, file transfer protocol client or web browser (Dolowitz, Buckler & Sweeney, 2008).

There are two types of search engines: first type is the search index which is a vast catalog made up of every word taken from all the web pages searched by crawler. Google is an example for this kind of search engines (Schwarts, 1998). Other type is the web directory is compiled by real people who organize web pages into categories and subcategories and they lets user to search very effectively. Yahoo is a kind of web directory and a good example for this kind of search engines. Most popular search engines are combination of these two principles (Cooper, Milner & Worsley, 2000). Today, Google is working as primary information resource of internet users (Ganzha, Paprzycki & Stadnik, 2010). If we check the statistics about search engines for last four years, we can see that Google and Yahoo! are leading the top search engines list since 2006. Since 2006, Google is the top and most used search engine. Yahoo! follows Google at the second place. Between 2006 and 2008, Msn/Live was the third most used search engine but in 2009, Msn/Live gave the place to their new and successful search engine Bing. These ranks determined according to the preferences of users. At the end of 2009,



Google is most used search engine, Yahoo! is the second one and Bing is the third one. Bing followed by Ask and AOLSearch is the fifth with (Hitwise Press Releases, 2010).

The Aim of the Study

The main purpose of this thesis is to find out which search engine is the most used one among university students. The study attempts to find answers to the following questions:

- 1. What are the search engine usage frequencies of students?
- 2. What are the students' criterions for search engine prefers?
- 3. What are the students' opinions about search engines?
- 4. What are the differences between search engines?

2. METHODOLOGY

Participants

The research was conducted at Near East University in Turkish Republic of Northern Cyprus during 2009-2010 fall semester and 300 voluntary students from 15 different faculties took part in the study. Twenty different students were selected randomly from each faculty with 20-22 age average. Faculties that took part in the research were Faculty of Atatürk Education, Faculty of Maritime Studies, Faculty of Law, Faculty of Economics and Administrative Sciences, Faculty of Communication, Faculty of Architecture, Faculty of Economics, Faculty of Health Sciences, Faculty of Medicine, Faculty of Performing Arts and Faculty of Tourism. Departments of students are Medicine, Computer Education and educational Teaching, Guidance and Psychological Counseling, Elementary Teaching, History Teaching, Deck, Maritime Business Administration and Governance, Dentistry, Pharmacy, Turkish Language and Literature, Psychology, Graphic Design, Law, Business Administration, Economics, International Relations, Computer Information Systems, European Union Relations, Radio-Television-Cinema, Journalism, Public Relations and Advertising, Architecture, Interior Design, Computer Engineering, Mechanical Engineering, Nursing, Nutrition and Dietetics, Theater, Author and Tourism and there are students from undergraduate, masters and PhD degrees.

Data Collection

"The Opinions of University Students about Search Engines" named questionnaire was prepared by the author and confirmed by 3 experts. The questionnaire has reliability Cronbach's alpha of 0.89. The questionnaire consisted of 3 parts. Part 1 aimed to collect personal information from the respondents with 6 questions. The part aimed to gather general information about some subjects like faculty, department and etc. Part 2 of the questionnaire consisted of 6 questions again and it is focused on gathering information about computer skills of respondent students. This part brought information about why and how students are using computer and internet. Part 3 of the questionnaire was about SE usage and it consisted of 9 questions. This last part reveals which SE is the most used one and why it is preferred. Also this part gathers information about complaints of students about search engines.

Data Analysis

During the survey, a questionnaire was used to collect data. After that SPSS 12.0 was used to analyze and interpret the collected data. Frequency, mean, standard deviation, one sample *t*-test and percentage methods were used during the analysis process. Mean difference is categorized from 1 to 6 as always used and never used.

	Always	Mostly	With	Rarely Use	Never	Never Use	Don't
	Use	Use	Another	·	Heard		Like
Google	74.30%	15.70%	9.30%	0.30%	0%	0.30%	0%
Yahoo	2.30%	5%	9.30%	20.70%	52.70%	1.30%	8.70%
Bing	0.30%	0.70%	3%	5.70%	51%	34.70%	4.70%
MSN/Live	4%	5%	13.30%	9.30%	49.70%	6%	12.70%
Ask	0.30%	0.30%	1.30%	3.70%	52.70%	36.70%	5%
AOLSearch	0.30%	0.30%	0.70%	1.70%	56%	36%	5.30%

3. RESULTS

	Always Use	Mostly Use	With Another	Rarely Use	Never Heard	Never Use	Don't Like
Google	74.30%	15.70%	9.30%	0.30%	0%	0.30%	0%
Yahoo	2.30%	5%	9.30%	20.70%	52.70%	1.30%	8.70%
Bing	0.30%	0.70%	3%	5.70%	51%	34.70%	4.70%
MSN/Live	4%	5%	13.30%	9.30%	49.70%	6%	12.70%
Ask	0.30%	0.30%	1.30%	3.70%	52.70%	36.70%	5%
AOLSearch	0.30%	0.30%	0.70%	1.70%	56%	36%	5.30%

Search Engine Usage of Students

According to Table 1, 74.30% of students always use Google. 15.70% of students stated Google as mostly used one. The Google is enough alone for students and only 9.30% use Google with another search engine if they can not find what they are looking for. Google is working as primary information resource of internet users (Ganzha, Paprzycki & Stadnik, 2010). This situation makes Google the most famous search engine for students in this research. With respect to Yahoo, 52.70% of students said that they never heard this search engine and 1.3% never used Yahoo. Only 2.3% indicate Yahoo as their favorite. On the other hand, results indicate that Bing has never been used by 34.70% of students and 51% of students indicating that they have never heard of such a search engine. 4.70% tried but did not like the Bing and only 0.30% indicated Bing as favorite. Furthermore, MSN/Live never been heard by 49.70% of students and 12.70% of students tried and didn't like it. Only 4% of students said they always use this search engine. The other search engine Ask have not been used by 36.70% of students and 52.70% of students never heard about this SE. Ask is favorite search engine of 0.30%. On the other hand, results indicate that 36% of students have never used AOLSearch as search engine and 56% have never heard of it. Exactly as Bing and Ask, only 0.30% chooses AOLSearch as favorite search engine.

Differences Between Search Engines

		nfidence l of the rence					
SEs	N	Mean	SD	Sig. (2-tailed)	Т	Lower	Upper
Google	300	1.37	0.69	0.00	34.15	1.29	1.45
Yahoo	300	4.55	1.25	0.00	62.98	4.41	4.69
Bing	300	5.29	0.86	0.00	106.39	5.19	5.39
Ask	300	5.38	0.77	0.00	120.54	5.29	5.47
AOLSearch	300	5.43	0.68	0.00	137.66	5.35	5.50
MSN/Live	300	4.64	1.47	0.00	54.68	4.48	4.81

Table 2: One-sample *t*-test for search engine usage frequencies among students

*Significant at the 0.05 level of confidence

According to the result of One Sample *t*-test for search engine usage of students, there is significant difference between selections of SEs. Google is the one which students always use with 1.37 mean differences. Beside Google, other search engines' means stacked between being rarely used search engine or never used search engine. Yahoo and MSN/Live are rarely used search engines with 4.55 and 4.64 mean differences. On the other hand; Bing, Ask and AOLSearch has never used search engine mean with 5.29, 5.38 and 5.43 mean differences.

Students Criterions for Search Engine Prefers

There are some factors which influence students in their preference of a search engine. These factors include homepage style, result page style, number of retrieved results, number of retrieved relevant results, popularity of search engines, and easy user interface (Bitirim, Tonta, Sever, 2002). Figure 1 represents students' most important preference criterions for this study.

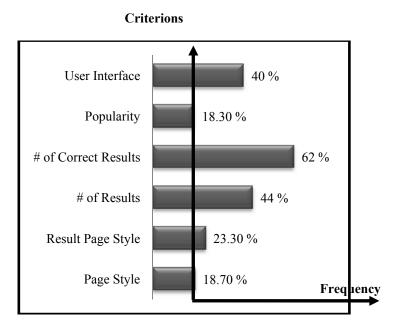


Figure 1: Important criterions for SE preferring

As Figure 1, the most important criterion for students is number of correct results with 62% frequency. Number of results is another important criterion and has 44% frequency. User interface has 40% frequency and it is another important criterion for students that influence them for search engine preferring. While result page style is important for 23.30% of students, 18.70% gives importance of page style. Popularity of search engine has the lowest importance with 18.30% frequency for students.

Students' Opinions about Search Engines

Opinions of students about other features of search engines are indicated in the Figure 5.3.

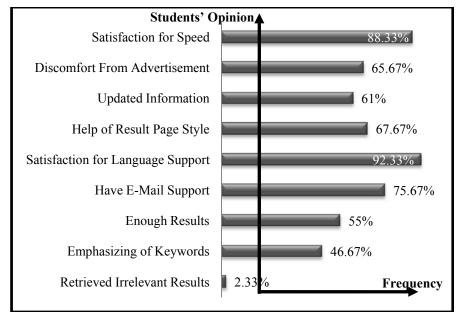


Figure 2: General opinions for search engines

As seen in Figure 2, students satisfied with the speed of their favorite search engine is a total of 88.33%. Nearly all search engines publish some advertisements, especially on the result page. Students evaluated the published advertisement on search engines and 65.67% of them underlined that advertisements bother them. 61% of



students feel that their favorite search engine is updated daily. As clarified before, style of result page is very important for user. Also 92.33% of students are satisfied from language support of their favorite search engine. 75.67% of students use e-mail support of their favorite search engine. 55% of students needs to see enough results at the end of their searches. Emphasizing of keywords helps 46.67% of students and 2.33% of students complains about retrieved irrelevant results during search process.

4. DISCUSSIONS, CONCLUSION AND RECOMMENDATIONS

In Near east University, Google is the most used search engine and Yahoo is the rarely used one but students generally have never heard of the rest of the SEs including Yahoo with 52.7%. These search engines are the ones that are leading the sector in the world but Near East University students may not well enough informed about these search engines. Exactly as in our study Tezer and Bicen (2009) stated Google as mostly used search engines in Near East University. Most important criterion for users is number of retrieved correct results and also number of results in another important criterion. Because user interface is another important criterion, homepage style and result page style is important as well. Overall results of this study add empirical data to the relevant field and are expected to help computer science students, experts, instructors, and everyone else who wants to reach information via the internet.

In addition, we can make the following proposals to future researches in this field:

- Some conferences or seminars may arranged by experts in order to give information to students about search engines.
- Spreading this research among universities in Cyprus.
- Applying the research on Turkish Republic universities.
- Applying the research on European universities.
- Increasing number of students.

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